RESEARCH IN HOLLAND

J. L. Snoek

New Developments in Ferromagnetic Materials

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"It is always a keen pleasure to read a booklet which is packed with new ideas and new knowledge, and for these reasons this little monograph is of the greatest importance to all interested in modern aspects of ferromagnetism...." *Science Progress*

MONOGRAPHS ON THE PROGRESS OF RESEARCH
IN HOLLAND DURING THE WAR

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Editorial Board

R. HOUWINK, DELFT; J. A. A. KETELAAR, AMSTERDAM

NEW DEVELOPMENTS IN

FERROMAGNETIC MATERIALS

*with introductory chapters on the statics
and the dynamics of ferromagnetism*

BY

J. L. SNOEK

NATUURKUNDIG LABORATORIUM DER N.V. PHILIPS' GLOEILAMPEN-
FABRIEKEN EINDHOVEN-HOLLAND

SECOND REVISED AND ENLARGED EDITION

CONTENTS

FOREWORD BY THE EDITORS

The purpose of this Series on the Progress of Research in Holland during the war is to show the world that scientists in the Netherlands have remained active during the five years of German occupation. The publication of monographs by the most representative research workers was already planned in the first years of the war, as a token of the undaunted spirit of the Netherlands.

In spite of the ever-growing burden of oppression and starvation research was continued intensively in all directions. Most of the material now published in this series was, for obvious reseasons, kept a secret during the war.

It being the Editors' aim to present these monographs as early as possible after the war, the majority of them were prepared whilst the war was still on. Authors were therefore expected to give mainly the results of their own investigations, without exhaustive reference to the Anglo-Saxon literature, which would not be available to them until after the war.

The hope is expressed that the publication of this series will further intensify the interest shown by the allied nations in the fate of the Netherlands, demonstrating, as it does, the whole-hearted preparedness of our nation to contribute to the progress of mankind.

The Editors wish to express their greatest admiration for the publishing house of Elsevier, which took very serious risk in preparing this series in wartime, when all activity on behalf of such international purposes was strictly forbidden.

The Editors,
DR IR R. HOUWINK
DR J. A. A. KETELAAR

Amsterdam, on V.E.-day, 8th May 1945.

Dr. J. L. Snoek

INTRODUCTION

There can be little doubt that the theory of ferromagnetic hysteresis in its present form — especially after the most useful extension given to it by M. KERSTEN — covers a wide field and is essentially correct. It is based on the two conceptions *crystal anisotropy* and *magnetostriction* and its principles are outlined in BECKER and DÖRING'S well known book on the subject.

Starting from these principles we have made an attempt to explain more fully the magnitude of the quadratic term in the Rayleigh relation, which has such important bearings on the hysteresis properties of materials used for communication purposes (c.f. §§ 1—5 and §§ 23—26).

Especially high values for μ_0, the initial permeability, and low values for H_c, the coercive force, may be expected, when both the crystal anisotropy and the magnetostriction are zero. In binary systems the exact coincidence of two „zero points" for these quantities will seldom occur. In ternary systems the "zero points" develop into "zero lines" and there is a possibility, that such lines intersect.

At the point of intersection we expect to find an alloy with high μ_0 and low H_c. Conversely if in a given ternary system the zero lines do not intersect, no exceptional properties are to be expected in any part of this system. By pursuing the course of the zero lines in all ternary systems consisting of metals, which are commercially available, J. J. WENT of this laboratory has aimed at obtaining a complete survey of the practical possibilities in this field. His interesting findings are briefly given in § 6; they have led to the discovery of a new alloy of the permalloy type (nickel manganese).

In BECKER's theory only two types of anisotropy are recognized, the one present in unstrained crystals and having the symmetry of the crystal and the other type which bears the symmetry of the elastic stress.

It is questionable, whether all possibilities have been exhausted in this way. In § 8 and 9 two cases of anisotropy will be recorded, which are not covered by either of the two conceptions used in the current theory. In the first case — Fe_3O_4 at low temperatures — the observed uniaxial anisotropy is most probably due to the 3 d-electrons assuming ordered positions in the lattice. In the second case (cold-rolled strips of nickel iron single crystals) the outward cause of the observed anisotropy, which is again of the uniaxial type, evidently is a plastic deformation, but it is not yet certain, whether the ions or the electrons (probably again by assuming ordered positions) are in the main responsible for the effect.

So much for substances which are on the whole to be considered as magnetically weak. When considering alloys with a high coercive force — such as $FeNiAl$, to take one of the technically most important alloys — it is likewise an open question whether the high magnetic strength can be accounted for by internal stresses alone (§ 10).

On account of the element "time" playing only a very subordinate role in hysteresis phenomena we have treated these subjects under the heading of *statics of ferromagnetism.*

Under the heading of *dynamics of ferromagnetism* resort

a. the influence of eddy currents on the magnetization process.

b. the various forms of magnetic after effect. To this may be added:

c. a phenomenon indicated by English scientists by the term "time decrease of permeability". (The French use the term "vieillissement réversible"). BECKER and DÖRING in recognition of the fact that a close connection of this effect with magnetic after effect was found by us to exist (Physica 1938, p. 663), propose the name: "after effect of the permeability". Its main features are a sharp rise in the initial permeability each time the sample is exposed to a change in the magnetic field, followed by a gradual and continuous decrease with time. In this book the name "disaccommodation" will be used and occasionally shortened to D.A.

The phenomena mentioned under *a* seem to touch a rather

well studied and threadbare subject. It will be shown, that this is not the case and that unexpected phenomena, due to eddy currents, may arise in ferromagnetics showing demagnetization (§ 11 and APPENDIX II.)

By far the greatest part of our attention will however be paid to the study of the magnetic after effect (occasionally shortened to M.A.), disaccomodation (D.A.), and to elastic after effect (occasionally shortened to E.A.).

Our researches in this field were started by the discovery in 1938, that well annealed samples of pure iron containing about a hundredth of one percent by weight of carbon or nitrogen display strong M.A., as well as D.A. and E.A.

The elastic effect is at the root of the magnetic phenomena. In 1938 we showed the connection between the three phenomena.

Part of our time during the war has been spent in testing in various ways the validity of the theoretical ideas developed at that time and shortly afterwards. A short note (§ 15) shows, that a supposed lack of harmony between the magnitude of the magnetic after effect and the elastic after effect does not exist and that our explanation of the magnetic effect in terms of magnetostrictive stresses leaves no shadow of doubt.

L. J. DIJKSTRA of this laboratory made more detailed experiments on the elastic after-effect. Single crystals of "Armco" iron produced by the method of critical stress were among the materials studied. It was found that the phenomenon is strongly anisotropic as predicted.

Also the relation between the magnitude of the effect and the lattice constants of tetragonal martensite was put to a test and a satisfactory agreement between theory and experiment obtained.

D. POLDER of this laboratory has put the theory into a more rigorous mathematical form. His results are found to be identical with those obtained by the author in 1940. It thus seems to be quite certain, that the after-effects are produced by the migration of ions of carbon and nitrogen in the lattice to and from certain places, the occupation of which produces a non spherical distortion of the lattice. In view of these

facts we propose to adopt in this book the name *ionic after-effect* for this class of phenomena.

Magnetic after-effect at higher frequencies (h.f. M.A.) has been studied occasionally on metals but so far little definite result has been obtained. The effect is of course intricately mixed up with eddy currents. Efforts to use the electric skin effect as a means of obtaining information on the magnetic properties at high frequencies are hampered by the fact, that the flux only enters an extremely thin surface layer of the material, where conditions may differ appreciably from those prevailing in the interior.

In this book a new approach to the problem is made. Part of the experiments relate to metals and form a continuation of work already reported in Physica **7** (1940) 515. We succeeded in obtaining direct confirmation for our anticipation, that very pure and well annealed iron shows a strong M.A. of the high frequency type at frequencies of the order of 1 kC/sec. This work gave a first indication of the fact that high values of μ_0 lead to increased relaxation times, which was repeatedly verified afterwards and theoretically accounted for later on.

A major impulse was however derived from the study of certain new materials already begun in 1933, which are non-metals (oxides) and have values of the specific electric resistance ranging from 10^{-2} *to* 10^{+7} *ohm. cm.* Eddy current effects in many samples of these "ferrites" are practically absent till frequencies of 1000 kC and higher.

These ferrites have the crystal structure of the well known mineral spinel $(MgAl_2O_4)$ and are therefore cubic, a feature allowing them in principle to develop high values for μ_0 after slow cooling from high temperatures similar to many cubic ferromagnetic metal alloys.

They are isomorphous with the well-known oxide of iron Fe_3O_4, magnetite or ferrous ferrite as it may be called. They may be considered to be derived from ferrous ferrite by replacing the ferrous ion by another bivalent ion M of about the same size (Mg, Zn, Ni, Mn, Co). The general formula thus is: $MO \cdot Fe_2O_3$.

In Chapter III the ferrites are discussed from a technical

point of view and their importance for high frequency work is pointed out. Numerous applications of these magnetic oxides are possible in radio and telephony.

The combined evidence obtained on non metals and on metals has led to a theory of the high frequency after-effects, the outlines of which are given in § 18. The term *electronic after-effect* has provisionally been adopted for this class of phenomena for reasons which are stated in the book. The testing of our ideas on the subject will no doubt take a long time and it is the hope of the author, that this task will be shared by other workers in the field. Much of what has been said in § 20 will sound premature to many readers and as yet not sufficiently founded upon facts. It is hoped however, that at least the heuristic value of the ideas exposed here will prove worth while and give a further impulse to the study of the transition metals and their oxides and perhaps to the study of the properties of solid substances in general.

As indicated by the title, this book though treating ferromagnetic materials is not meant to give in the first place a comprehensive survey of the whole field. Primarily it is intended as a report on our researches during the war under conditions which became gradually harder and in an atmosphere ill suited to the development of scientific thought.

I. STATICS OF FERROMAGNETISM

§ 1. THE GENERAL THEORY OF FERROMAGNETIC HYSTERESIS

The phenomenological theory [1] of hysteresis starts from the empirical fact, that in almost every ferromagnetic material there is a certain interaction between the spins and the lattice, as a result of which certain "preferred directions" for the direction of magnetization arise. The work required to turn the spins in one - cm^3 of the substance from the direction of minimum energy to the direction of maximum energy will be called the *anisotropy energy* of the substance and indicated by the symbol E_A. It is not to be confounded with the *interaction energy* E_I, which measures the energy required to bring one cm^3 of the substance from the ferromagnetic into the paramagnetic state. For reasons of simplicity each point of the ion lattice is supposed to be the seat of one elementary spin. The lattice is assumed to be cubic and to have a lattice constant a.

As shown by F. BLOCH the existence of an energy E_A different from zero leads under certain conditions to the formation of zones — the so-called Bloch zones — in which the direction of magnetization varies from one direction of minimum energy to another. The zone has a thickness given by

$$\delta = a \sqrt{\frac{E_I}{E_A}} \tag{1}$$

and is the seat of a surface energy, the magnitude of which per cm^2 is given by

$$\gamma = 2\, E_A \cdot \delta = 2a \sqrt{E_I \cdot E_A} \tag{2}$$

To find the total surface energy E_0 of a given zone we have to multiply γ by a factor $O_{\text{act.}}$ indicating the active surface of the zone, so that

[1] Cf. R. BECKER AND W. DÖRING's book *"Ferromagnetism"*, Berlin 1939, in the following cited as B. and D.

$$E_0 = \gamma \cdot O_{\text{act}} \cdot \qquad (3)$$

As pointed out by KERSTEN [1] it is important to remember that O_{act} may be smaller than the true surface of the zone, especially if the material contains holes or unmagnetic inclusions, because places where the zone cuts an inclusion are not the seat of a surface energy such as indicated above.

In the course of the past ten years it has become increasingly evident that hysteresis is due to strong local variations in the surface-energy stored in the Bloch zones. For instance the specific energy γ may show local variations due to the presence of internal strains, influencing the value of E_A.

E_A is usually looked upon as consisting of two terms, a term E_c the so called *crystal anisotropy*, which is characteristic of the undeformed crystal, and a term $\lambda\sigma$, the *stress anisotropy* (σ the stress, λ the magnetostriction constant). E_c in a homogeneous material is a constant and so does not contribute to variations in γ.

A variation $\Delta\sigma$ of about 5 kg/mm² in the internal stress must be considered to be present inside every commercial iron alloy in the annealed state. These stresses can be made "inactive" only by choosing a material for which λ is very small. Positive as well as negative values of λ occur in both crystal lattices, which are important for ferromagnetism (the cubic body centered and the cubic face centered lattice) and mixed crystal formation takes place to a large extent between metals having the same lattice type. It is therefore possible in principle to make λ zero by choosing a suitable proportion of materials with a positive λ and a negative λ respectively. For non-metals (ferrites) the same reasoning has been found to be applicable.

As pointed out by KERSTEN not only γ, but also O_{act} may show local variations as a result of the presence of unmagnetic (or weakly magnetic) inclusions. Imagine these inclusions to be little spheres, placed on the points of a simple cubic lattice

[1] M. KERSTEN, *Phys. Z.*, **44** (1943) 63, and from the same author: „Grundlagen einer Theorie der ferromagnetischen Hysterese und der Koerzitivkraft, Leipzig 1943, in the following cited as "Grundlagen".

of parameter s; it is easily shown, that

$$\frac{d}{s} = \left(\frac{6}{\pi}\right)^{1/3} a^{1/3}$$

where a is the (volume) percentage of the minor constituent, and d the diameter of the (spherical) inclusions. In technical materials a may vary between 10^{-3} and 10^{-4} and d/s is thus found to be of the order 0.1. The quantity d/s will return in our discussion more than once.

Even without any calculations it will be clear that variations in O_{act} will be just as effective in causing hysteresis as variations in γ, even if the effect of stresses is eliminated by choosing λ small, for as seen above E_A does not only contain the term $\lambda \cdot \sigma$, but also the (constant) term E_c, the crystal anisotropy. Only by choosing E_c zero simultaneously with λ, γ as well as $\dfrac{d\gamma}{dx}$ become very small and there will be no appreciable hysteresis.

For E_c also positive as well as negative values have been observed and zero points can be obtained in any binary system, where both signs of E_c occur inside a region where mixed crystals are formed.

The simultaneous fulfilment of both requirements

$$\left.\begin{array}{l} \lambda = 0 \\ E_c = 0 \end{array}\right\} \tag{4}$$

in a binary alloy or in a binary mixture of non-metals will in general be impossible or at any rate highly improbable.

The well-known alloy permalloy is an example of a binary alloy, for which the above requirements are approximately fulfilled. The measure to be taken is evident: *by adding a third component to a binary system the zero points are drawn out into zero lines, the course of which may be followed inside a ternary system. At the points of intersection of these curves very low values of the hysteresis are to be expected.* We will return to these questions in § 6.

Quite apart from the possibilities indicated above we are interested in the relative magnitude of the hysteresis effects brought about by one of the quantities λ or E_c being different from zero.

In order to be able to discuss this question we first require a short treatment of the two models, in which both types of hysteresis are realized as purely as possible.

§2, THE INCLUSION MODEL [1]

The anisotropy energy and consequently the specific surface energy are assumed to be constant throughout the material. The condition required for equilibrium in a situation as represented by Fig. 1 is given by (5).

$$H = \frac{\gamma}{I_{max}} \cdot \frac{1}{O} \cdot \frac{dO}{dx}, \quad (5)$$

where H stands for the magnetic field, I_{max} for the saturation magnetization and O for O_{act}. From (5) we find for the critical field H_0 and the initial susceptibility χ_0

$$H_0 = \frac{\pi d}{s^2} \cdot \frac{\gamma}{I_{max}}, \quad (6)$$

$$\chi_0 = \frac{\beta}{2} \cdot \frac{s}{\pi} \cdot \frac{I^2_{max}}{\gamma}. \quad (7)$$

In equation (7) β denotes the fraction of the energy minima which is actually occupied by a Bloch zone.

We note in passing that in this model the susceptibility is rigorously constant up to the critical field H_0. The limiting value of the induction B_1 below which no hysteresis occurs is found from (6) and (7) to be equal to

$$B_1 = \tfrac{1}{2} \cdot \beta \cdot \frac{d}{s} \cdot P_{max}. \quad (8)$$

[1] Cf. Appendix I, p. 106.
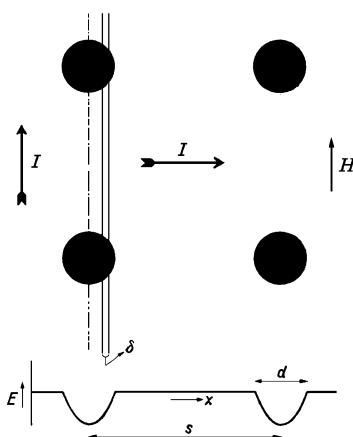
Fig. 1

Inclusion model of ferromagnetic hysteresis.
I = direction of the magnetization. H = direction of the magnetic field. The black circles represent inclusions arranged along a simple cubic lattice. The potential energy has a minimum. where a Bloch zone (indicated schematically in the figure by two parallel lines at distance δ) cuts the spherical inclusions in an equatorial plane. The diameter d of these inclusions being small in respect of the distances between them, the width of the potential minima and consequently the reversible displacement of the Bloch zones is relatively small.

§ 3. THE STRESS MODEL

The anisotropy is assumed to be of the uniaxial type, the direction along which the energy is minimum being the same throughout the material, but certain fluctuations in the absolute value of the anisotropy energy E_A are supposed to exist, as a result of which γ is a periodic function (with period l) of the place in the lattice [1]. Equation (5) now changes into

$$H = \frac{1}{2I_{\text{max}}} \cdot \frac{d\gamma}{dx} \tag{9}$$

while (6) and (7) are replaced by

$$H_0 = \frac{\pi}{2} \cdot \frac{\lambda \cdot \varDelta\sigma}{I_{\text{max}}} \cdot \frac{\delta}{l}, \tag{10}$$

$$\chi_0 = \frac{\beta}{\pi} \cdot \frac{I_{\text{max}}}{H_0}. \tag{11}$$
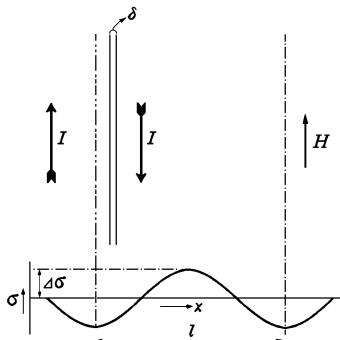
Fig. 2.

Stress model of ferromagnetic hysteresis.
The stress is supposed to vary as a sine with amplitude $\varDelta\sigma$ around a fixed amount σ_0, $\varDelta\sigma$ being very small compared to σ_0. The width of the potential minimum for the Bloch zones is comparable to the length l of a mean period. The other symbols have the same meaning as in Fig. 1.

Contrary to the results found for the inclusion model the susceptibility is not found to be constant for all field strengths below the critical value, but becomes larger in the immediate neighbourhood of this value. In view of much larger effects to be discussed later we will disregard this detail and again ask for the limiting value of the induction, below which no hysteresis occurs. It is

$$B_1 = \frac{1}{\pi} \cdot \beta B_{\text{max}} \tag{12}$$

and thus larger than (8) by a factor s/d.

[1] M. KERSTEN, "Probleme der technischen Magnetisierungskurve", Berlin 1938, 54.

§ 4. HYSTERESIS AT LOW VALUES OF THE INDUCTION

Cables used for telephony are provided at regular intervals with so-called "loading coils", self-inductances, and mutual inductances of about 60 mH [1]. It is important, that these loading coils, of which large numbers are required, shall be as small as possible. To that end the coils are provided with a ferromagnetic core with a permeability aimed at values between 30 and 120, according to the special purpose in mind.

The inevitable increase in the total losses and a certain amount of non-linear distortion should remain between certain well specified limits, if the apparatus is to be workable. The reduction of the distortion is the bigger problem of the two and in the following we shall look at this problem a little closer. Let V be the voltage on the coils under working conditions. The second induction law tells us, that V is related to B_0, the top induction in the core, by something like

$$V = N^2 . O . \omega . B_0, \qquad (13)$$

where N is the total number of windings on the coil, O the surface of a transverse section of the core, ω the circular frequency. Unimportant numerical constants in this relation are omitted. N^2 must exceed a certain lower limit, because otherwise the current required to produce a certain induction would become too large. It is evident that a diminution of O, which would allow us to reduce the volume of the core, can only be brought about by making B_0 larger. On the other hand the non-linear distortion rises as B_0 rises, and it is clear that a material will be the better suited to telephony purposes, the higher the value of B_0, which it can stand without the distortion becoming unduly high.

Making a comparison on that basis between the inclusion model and the stress model, it at once follows from (8) and (12) that unmagnetic inclusions are in general more harmful than internal stresses because of the factor d/s which as said before often is in the neighbourhood of 0.1.

[1] Jhr. W. SIX, J. L. SNOEK AND W. BURGERS, *De Ingenieur*, 1934, E 195—200.

We shall now discuss the validity of our argument.

Further consideration and the graphs of Fig. 1 and 2 immediately make clear on which assumptions our conclusion is based. The amount by which a Bloch zone can be displaced, without leading to a discontinuity, is of the order of the ratio of the width of a potential minimum to the period of that potential. We thus see, that our general conclusion is in the end based upon our tacit assumption that the internal stresses roughly vary as a sine throughout the material, whereas the smallness of the diameter of the inclusions with respect to the distance between them causes the potential minimum in the inclusion model to be relatively sharp. It follows that our conclusion would become invalid, if it could be shown that (a) the internal stresses are of another type than has been assumed or (b), that the ratio d/s would be much larger than 0.1. There seems to be no reason at all, however, to doubt these basic assumptions. An interesting consequence is, that for substances with a large crystal anisotropy it may be found useful to increase the volume percentage a of the inclusions, because the factor d/s will be raised by such a measure.

In comparing (8) and (12) we have tacitly assumed the values of $I_{\max}$ and β to be equal for the two cases. It is clear that a high value of these factors will in general be favourable. Other circumstances being equal the material with the higher saturation value is therefore to be preferred. To say something about β is more difficult. It is at once seen, that it is this factor which really rounds off the sharp corners of our statement that the inclusion model leads to the largest hysteresis values. For if d/s would be made very small, conditions would probably in the end be such that Bloch zones would be found also in other places than those prescribed by the inclusions.

The whole matter is summarized in the following statements:

$a.$ the mean period of the disturbances is within wide limits without any influence on the result.

$b.$ other circumstances being equal the material with the higher value of $I_{\max}$ is to be preferred.

$c.$ the hysteresis factor of a material containing only traces

of impurities will be highly dependent upon the number of occupied "inclusion" minima, as compared with the number of "stress" minima and will be higher, the higher the former.

d. for special materials with an abnormally high value of d/s conclusion c is not valid.

e. a reduction in the size of the Weiss domains is favourable for obtaining low hysteresis coefficients.

It is the last conclusion really, which for the present does not allow us to clinch the whole matter into numerical relations and easily predictable results. We shall return to this matter in Chapter III.

§ 5. Rayleigh's relations

The fact that neither the inclusion model nor the stress model does lead to the well-known relations deduced by Rayleigh for the hysteresis [1] might be looked upon as a deficiency in these models.

This deficiency is not as serious as it would seem to be at first sight. It is easily understood why our two models fail in this respect: this is chiefly due to the highly artificial assumption, that the distribution of the stresses and the inclusions in space are strictly periodical. Only by assuming this we find that the Bloch zones become flat surfaces, falling straight into the pits dug for them by the studious modelmaker. In reality conditions are very different. The Bloch zones will in general be curved and the zones will not be allowed fit themselves into the potential minima as snugly as was assumed. It is qualitatively clear, that parts of the zone will be in a very unstable position, the least shock leading to a discontinuous correction of the form of the zone. Statistically, however, such a situation will be a rare occurrence and accordingly non-linear distortion at low values of B and H will be very small.

[1] *Phil. Mag.*, [5] **23** (1887) 225; cf. W. B. ELLWOOD, *Physics*, **6** (1935) 215; E. PETERSON, *Bell Syst. Tech. Journ.*, **1** (1928) 75 and V. E. LEGG, idem **15** (1936) 39.

The task of finding a suitable generalization of the original hysteresis models, leading to a model obeying the Rayleigh relation, is essentially a statistical problem, the difficulties of which are admittedly great but do not seem insuperable.

Of course not only the period but also the amplitude of the disturbances will in practice not be strictly constant throughout the material. This is considered however to be a factor of minor importance. There is no need of introducing a generalization of this kind into the model.

Finally returning to our conclusions, drawn from a comparison of the two types of hysteresis, it is to be noted that the influence of the rotation in a domain as a whole has not yet been for account. Only the lateral displacements of the Bloch zones have been taken into consideration.

It is easily shown that if these processes are taken into account, the inclusion model compares even more unfavourably than before.

It may thus be expected that the rules stated above will prove to be of some value in analysing results obtained in practice on materials having widely different values of I_{max}, E_c, λ, $\Delta\sigma$ and d/s. Such an analysis will be tried in Chapter III.

§ 6. Zero lines of crystal anisotropy and magnetostriction in ternary systems

The importance of zero lines of E_c and λ in the search for alloys with a low hysteresis has already been alluded to in section 1. The regrettable fact that λ unlike E_c is not a simple constant for any alloy, but may depend upon the direction of magnetization relative to the crystal axes, was not mentioned then, but obviously represents a complication.

For various alloys WENT has plotted the magnetostriction against the field and where the curve of this line suggests that λ is strongly anisotropic, has extrapolated the curve in

such a way, that a probable value for λ in the direction of minimum energy was obtained. This procedure is obviously not
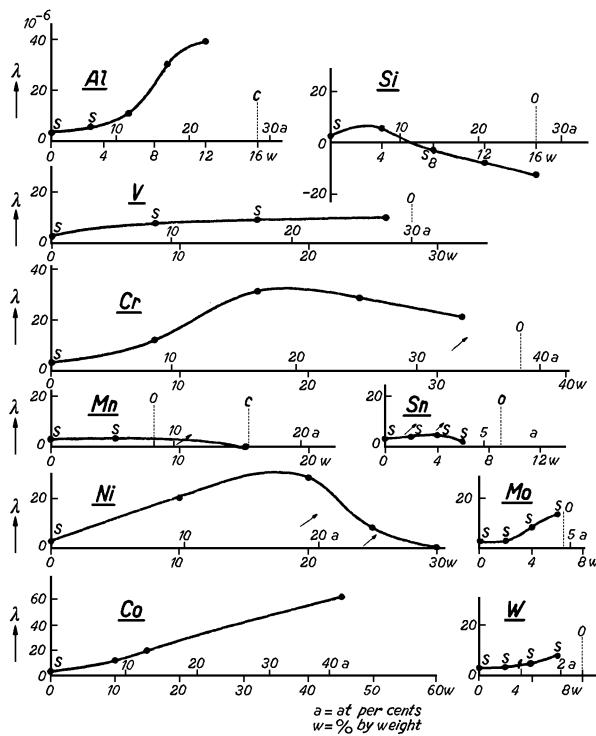
Fig. 3.

Measured values of the magnetostriction λ in binary systems, having iron as a main component. An arrow indicates cases, where the volume magnetostriction is found to be high.

entirely satisfactory, but it was the only way leading to practical results in a short time.

Once λ has been determined, $\lambda \Delta\sigma$ can be calculated, provided we know $\Delta\sigma$. As pointed out in the first section the assumption that the mean value of $\Delta\sigma$ is equal to 5 kg/mm^2 in well-annealed iron alloys of commercial quality seems not

to be far from the truth at any rate it has in no case led to contradictory results.

The specimens used for the determination of λ had the form of small bars of 10 cm length, having a diameter of about
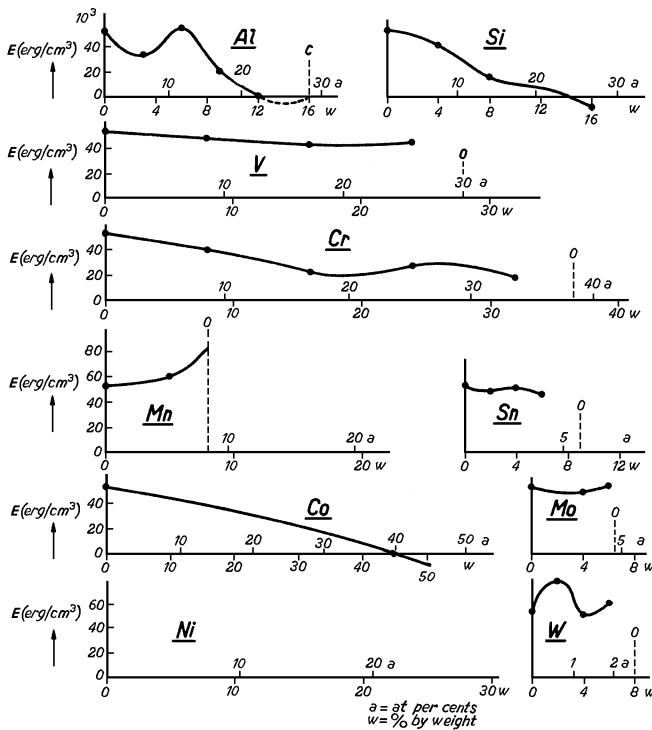
Fig. 4.

As Fig. 3, but this time the magnetization energy E (corrected for the term λ . $\Delta \sigma$) is the measured quantity. Points, where the alloy becomes heterogeneous are marked by 0; points where ferromagnetism ends by C.

2.5 mm. They were poured from the melt into dies holding small tubes of a special glass, thus yielding a perfectly smooth surface. No sticking of the glass to the metal occurred except in one case (where vanadium was added). Afterwards the glass was broken off. Conditions of casting were such, that

no large anisotropy in the bars was to be expected as indeed proved to be the case on testing them by X-rays.

The main component in the first part of the investigation was iron. To this element the commercially available elements $Al, Si, Sn, V, Cr, Mn, Co, Ni, Mo, W, Zn$ were added, the more costly elements being left out on account of their purely academic interest.

The crystal anisotropy was calculated from the form of the ideal magnetization curve as measured on the same samples, and a correction for the magnetostriction energy $\lambda \cdot \Delta\sigma$ was each time applied along the lines indicated.

In order to find zero lines for E_c and λ, zero points in the binary systems must be available first. Fortunately part of this work had been done on the more important binary systems already[1], thus yielding also data for the sign of E_c, which can of course not be found from measurements on polycrystalline specimens. Once the sign of E_c on one side of the triangle representing a ternary system is known, the determination of the correct sign inside this system usually presents no insuperable difficulties.

Fig. 5.

E_c in the ternary system Fe-Si-Al. Curve represents concentrations for which the crystal anisotropy is zero.

A survey of the results obtained for E_c and λ in binary

[1] J. W. SHIH, Phys. Rev., 46 (1934) 139; J. D. KLEIS, ibid., 50 (1936) 1178; F. PREISACH, Ann. d. Phys., 3 (1929) 737; K. HONDA AND K. KIDO, Sc. Rep. Tôhoko University, 9 (1920) 221; L. P TARASOV, Phys. Rev., 56 (1939) 1224 and 1245.

systems (Figs. 3 and 4) shows that the number of zero points and consequently the number of zero lines is very limited: only Si causes λ to change sign. With E_c the three elements Al, Si and Co have the same effect. In this way the ternary systems Fe-Si-Al and Fe-Si-Co present themselves as the only ones worthy of further inspection.

Fig. 5 and Fig. 6 give the course of the zero lines as drawn by WENT for the ternary system Fe-Si-Al, based upon an accurate inspection of the admittedly scarce data. It is satisfactory to find that the point of intersection corresponds with the maximum in the permeability observed by MASU-MOTO in 1936 for these alloys [1].
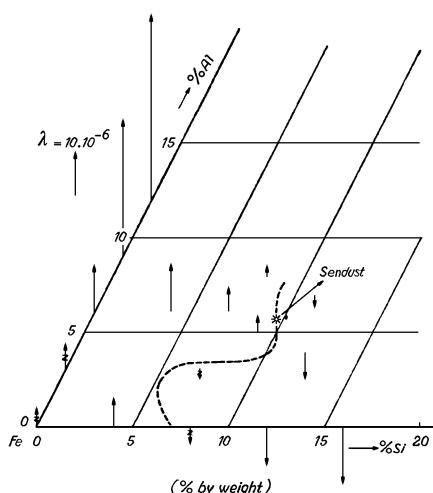
Fig. 6.
λ in the ternary system Fe-Si-Al. The curve represents concentrations for which $\lambda_r (\lambda$ in the direction of preferred magnetization) is zero.

Theory and experiment seem to agree within the accuracy of the data. A control determination of the sign of the (rather weak) crystal anisotropy on the other side of the zero line, where it is negative according to the diagram, would involve the preparation and handling of single crystals of the required composition. These single crystals were obtained with ease, but we have not been able to make satisfactory ellipsoids of them.

It is worth while noting that on the zero line for E_c the

[1] H. MASUMOTO, *Sci. Rep. Tôhoko University*, **25** (1936) 388 (Honda Vol.).

Curie point according to determinations by the author lies between 400 and $500°$ C.

Inspection of the zero lines in the ternary system *Fe-Si-Co* (Fig. 7 and Fig. 8) shows that these curves do not intersect. Consequently no high μ-alloys are to be expected in this ternary system.

Starting with pure nickel the cubic face centered alloys were
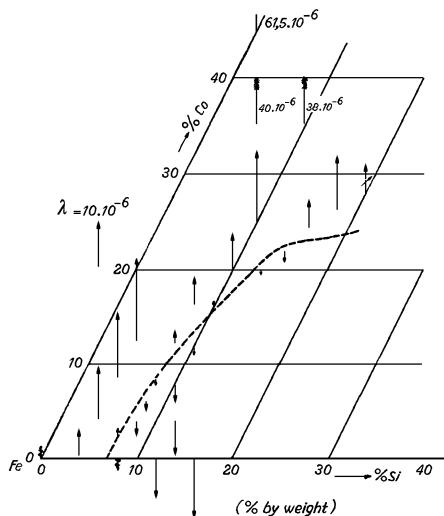
Fig. 7.
λ in the ternary system *Fe-Co-Si*.
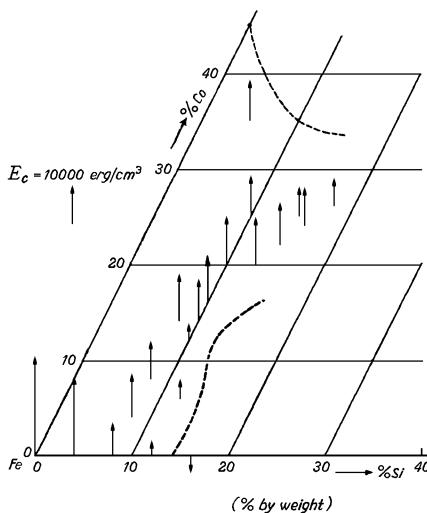
Fig. 8.
E_c in the ternary system *Fe-Co-Si*.

attacked in the same way and by the same methods as were the body centered alloys. Unfortunately the frequent occurrence of a tendency towards ordered arrangements complicates matters here as does the fact that E_c proved to be very small compared with $\lambda \, \varDelta \, \sigma$ in the region investigated. Consequently the results are still too uncertain to justify publication now.

One new and interesting result was obtained on a binary alloy: nickel containing 19% of manganese, when in the ordered state[1], proves to have E_c and λ zero and consequently is a

[1] Cf. A. KUSSMANN, *Z. Metallk.*, **31** (1939) 212.

high μ-alloy. Values of 8000 for μ_0 and 0.04 for H_c have been obtained with ease for these alloys, using commercial materials.

The question has often been discussed, whether a tendency towards an ordered arrangement in a ferromagnetic alloy leads to increased hysteresis or not. Basing our conclusions upon the results mentioned above, we are now able to say that such a statement is without any point.

The only thing which really matters is that order leads to an alloy having magnetic and other properties which may differ considerably from the properties of the unordered alloy.

Whether the ordered alloy or the unordered alloy is magnetically the weaker one, is entirely a matter of chance.

As a matter of fact, now that a complete survey of occurrences in commercially available materials has been made, we find that, of three possible cases, each has been realized exactly once. We have:

a. a case, in which the ordered alloy is the magnetically weaker one (nickel manganese).

b. a case, in which a certain amount of disorder is essential to fulfil the conditions $E_c = 0$, $\lambda = 0$ simultaneously (permalloy).

c. a case of a magnetically weak alloy, in which no ordering occurs at all (sendust).

§ 7. Permeability and coercive force of the cubic ferromagnetic oxides

So far little systematic study has been made of the magnetic properties of non-metals. Yet the study of these is especially attractive, because these substances have a much larger specific electric resistance than the alloys and accordingly particularly low eddy current losses. The idea, that such ferromagnetic non-metals might be useful as a core material for high frequency cores, is almost as old as the systematic study of ferromagnetism itself; G. Hilpert [1] took out a number of patents in 1909 on the use of ferrites for this purpose.

[1] D.R.P. Nr. 226347 and Nr 227787.

The only ferrite occurring in nature in the form of fairly large single crystals is the well-known ferrous ferrite $FeO \cdot Fe_2O_3$ ($= Fe_3O_4$) or magnetite, as it is commonly called. Its saturation value, its Curie point and its crystal anisotropy were determined long ago by that pioneer of magnetic investigations, PIERRE WEISS, in a series of careful measurements [1].

The value of I_{max} for magnetite is of the same order as that of nickel, while the crystal anisotropy according to V. QUITTNER can be estimated to about — 100,000 erg/cm³. The magneto-striction was determined by WENT on a polycrystalline specimen, prepared by the reduction of a pressed bar of Fe_2O_3 in nitrogen at 1350° C. It was found to be about as large as the values obtained on polycrystalline nickel ($+ 37.10^{-6}$) but to have a positive sign. The particular importance of this fact will become clear when we have discussed the properties of other ferrites. Values of the permeability and the coercive force obtained on various samples of Fe_3O_4 did not differ much from those obtained on nickel, which is according to expectation.

The chemical formula of other ferrites may be obtained by substituting for the ferrous oxide another oxide of a bivalent metal. The ionic volume must not fit too badly into the original structure (which is of the spinel type) [2].

Substances such as $MgO \cdot Fe_2O_3$ are well defined chemical substances, which may be prepared by intimately mixing the finely divided oxides in the required proportion and heating the mixture above 800° C. Ni and Co are known sometimes to have valencies different from two, but nevertheless substances having the approximate composition $NiO \cdot Fe_2O_3$ and $CoO.Fe_2O_3$ are easily obtained.

As may be expected, more trouble is experienced in the attempt to make such substances as $CuO.Fe_2O_3$ or $MnO.Fe_2O_3$

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[1] P. WEISS, *Thèse*, Paris 1896; *J. Phys.*, [3] 8 (1896) 435 V. QUITTNER, *Ann. der Phys.*, **30** (1909) 289; P. WEISS AND R. FORRER, *Ann. d. Phys.*, **12** (1929) 297.
[2] H. FORESTIER, *Comptes Rendus Paris*, **192** (1931) 842.

because of the strongly variable valency of the Cu and the Mn ion [1].

All ferrites at temperatures above 1200°C suffer a slight dissociation, part of the iron changing from the trivalent into the bivalent form. This tendency is particularly strong, if more Fe_2O_3 is added than corresponds to the chemical formula of an ordinary ferrite. If the degree of dissociation is suitably chosen, such a mixture may be looked upon as a mixed crystal of an ordinary ferrite with Fe_3O_4, as will be easily realized.

The very short discussion on the chemical side of the problem given above is necessary in order to understand the results of our magnetic investigations.

The first discovery with respect to the ferrites concerns the Curie temperature and the adaptation of the latter to such conditions, that a much larger value for the initial permeability could be realized than was hitherto thought possible for these substances.

Of all ferrites satisfying the conditions mentioned above, only the one with zinc is unmagnetic at room temperature. The ferrites under discussion mix freely and without any limitation on the proportion of the components. It has been found that by the addition of Zn ferrite to a magnetic ferrite the Curie temperature can deliberately be lowered to a temperature slightly above room temperature. By this measure the maximum in μ_0, usually observed just below the Curie point, may be shifted till it lies just at room temperature and in this way high values of μ_0 may be realized. The results obtained will be discussed in Chapter III.

In this connection another point is of particular interest, which will also reappear in Chapter III.

From the study of the alloys it is known that both the crystal anisotropy E_c and the magnetostriction λ diminish on approaching the Curie point. However E_c has usually become

[1] J. L. SNOEK, *Physica*, 3 (1936) 463; A. E. v. ARKEL, E. J. W. VERWEY AND M. G. VAN BRUGGEN, *Rec. Trav. Chim. Pays Bas*, 55 (1936) 331.

C. WIJCKOFF, *X-rays and Crystal Structure*, Suppl. 1930 – 1934 p. 64.

practically zero long before the substance has become unmagnetic [1], while λ remains different from zero right up to the Curie point [2].

Most probably by reducing the Curie point, we have "killed" the crystal anisotropy E_c of the ferrite. In order to obtain full results as to permeability and coercive force we should have an additional means of "killing" the magnetostriction λ and so obtain a really high μ-ferrite.

It now turns out on closer inspection that these means exist.

Measurements on the magnetostrictive properties of the ferrites revealed the interesting fact that all the the "single" ferrites have negative λ, except ferrous ferrite or Fe_3O_4. Taking into account again that mixed crystal formation is possible without any limitation between the ferrites mentioned, the discovery that by addition of Fe_3O_4 to any ferrite or mixture of ferrites small values of λ are occasionnally obtained, can be understood. If Fe_3O_4 is added to the mixtures of magnetic ferrites with zinc ferrites mentioned above, we should obtain homogeneous ferromagnetic substances, fulfilling at the same time the condition $E_c = 0$ and $\lambda = 0$. (Provided E_c behaves sensibly as a function of the temperature and λ is not too strongly anisotropic). It was stated above that ferrites containing Fe_2O_3 in excess easily dissociate on heating at high temperatures, forming Fe_3O_4, which is readily taken up by the lattice. All ferrites however, also the stoechiometric ones, suffer a slight dissociation at high temperatures and this fact influences the results obtained on these ferrites after annealing them at increasing temperatures.

Practical difficulties are of course numerous, e.g., carrying the dissociation to the right degree and just as far inside the specimen as near the surface, preventing the sample from taking up oxygen again on cooling, etc.

The principles according to which one may work, have however been outlined above.

It is seen on the one hand that the conditions for obtaining

[1] Cf. B. and D. p. 125.
[2] Cf. B. and D. p. 132.

high μ_0 and low H_c for the non-metals are identical to those found to exist for the metals.

On the other hand the search for "zero points" and "zero lines" for the ferrites has been obviated by making use of the relatively simple laws governing λ and E_c.

§ 8. Fe_3O_4 AT LOW TEMPERATURES

The formal theory of ferromagnetism operating with the two notions *crystal anisotropy* and *magnetostriction* knows of no anisotropy forces inside a ferromagnetic having a lower symmetry than the crystal itself.

On the contrary the expectation that the symmetry of ferromagnetic anisotropy should at least be equal to that of the crystal, forms the keystone of the phenomenological theories developed by BECKER and KERSTEN. In crystallography the above rule, which seems fairly evident in itself, is known by the name "NEUMANN's principle".

It is the more remarkable that a number of exceptions to this rule exist and that one of them was discovered as early as 1932, i.e., shortly after the theories of BECKER and KERSTEN were published, without apparently anybody noticing the paradox or drawing the consequences.

CHING HSIEN LI [1] (working at that time in the laboratory of L. W. MC KEEHAN) proved, that single crystals of magnetite when cooled below 114.5 °K developed a strong ferromagnetic anisotropy, the direction of the magnetic field during cooling determining the axis along which the magnetic energy is minimal. CHING's experiments have been repeated by us on polycrystalline specimens of Fe_3O_4. His results were fully confirmed.

The low value of the transition temperature combined with the fact, that the crystal will withstand the phase transition several times without any damage or distortion, make it highly improbable that the ion lattice would undergo any change of symmetry there. This point was confirmed by making Laue

[1] CHING HSIEN LI, *Phys. Rev.*, **40** (1932) 1002.

photographs above and below the transition point (SHÔJI in 1935) [1].

The transition itself, judging from determinations of the specific heat by R. W. MILLAR [2], is not really discontinuous but covers an interval of at least $15°$ C (Cf. Fig. 9)

Magnetic observations seem to indicate that the effect of the low temperature transition even stretches over a considerably larger region of temperatures. We have measured the initial
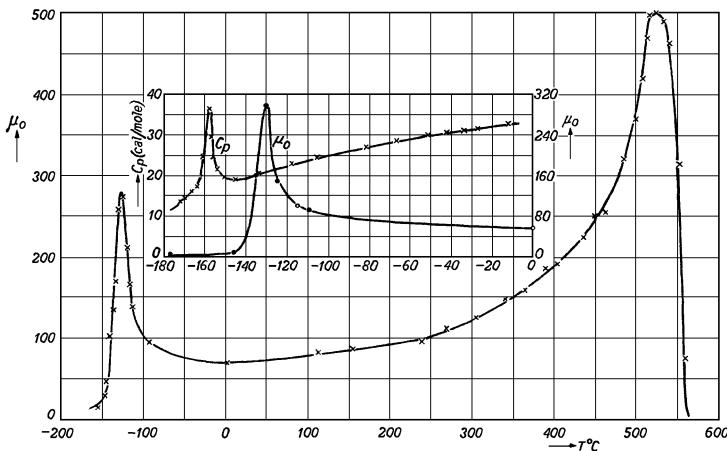
Fig. 9.

μ_0 vs T for sample of Fe_3O_4 prepared by the reduction of Fe_2O_3 in nitrogen at $1300°$ C. The maximum in C_p found by R. W. MILLAR at $-160°$ C is also reproduced in the figure.

permeability of a number of samples of Fe_3O_4, most of them made by reducing pressed bars of Fe_2O_3 at $1300°$ C in nitrogen (Fig. 9). Two maxima in μ_0 are clearly visible in all these curves: one, the normal one, lies immediately below the Curie point; the other one just above the temperature where the magnetic anisotropy changes its character. A most remarkable feature about this second maximum is, that the abnormal rise in μ_0 with decreasing temperature sets in already just below $0°$ C,

[1] HIKOROKU SHÔJI *Sci. Rep. Tôhoku University*, **24** (1935) 250.
[2] RUSSEL W. MILLAR, *Journ. Am. Chem. Soc.*, **51** (1929) 215.

i.e., a hundred degrees from the temperature where the phase transition is supposed to take place.

E. J. W. VERWEY of this laboratory working with J. H. DE BOER on the semi-conductive properties of Fe_3O_4 put forward the theory [1], that its rather high conductivity might be due to the existence of several equivalent positions in the lattice available to the 3 d-electrons. From this point he developed the idea that what really happens in Fe_3O_4 at temperatures of about 114.5° K, is the formation of an ordered arrangement of these electrons. The inevitable consequence, that the conductivity would show a very large drop at that temperature was fully confirmed first by VERWEY himself, and later more carefully by VERWEY and HAAYMAN (E. J. W. VERWEY Nature, 144 (1939) 327; E. J. W. VERWEY and P. W. HAAYMAN Physica 8 (1941) 979).

We see here a possible connection between ferromagnetic anisotropy and the positions the electrons occupy in the lattice.

The combined experimental evidence on the properties of Fe_3O_4 at low temperatures perhaps offers a better clue to the understanding of the nature of ferromagnetic anisotropy than any observations made so far on metal crystals.

Magnetite is not the only example of a substance having a ferromagnetic anisotropy, the symmetry of which is not in accordance with the symmetry of the lattice. We shall discuss another case in the next section.

§ 9. EFFECT OF COLD ROLLING ON THE PROPERTIES OF ALLOYS OF NICKEL AND IRON

This effect was first studied by the author in 1935. After this the matter has been dealt with again at length by G. RATHENAU and the author (Magnetic anisotropy phenomena in cold-rolled nickel-iron, *Physica*, 8 (1941) 555).

It would carry us too far to review here in detail the experimental evidence brought forward in these publications. It is sufficient to say, that the anisotropy phenomena observed on cold-rolled nickel iron alloys have been reduced to the

[1] E. J. W. VERWEY AND J. H. DE BOER, *Rec. Trav. Chim. Pays Bas*, **55** (1936) 531.

simplest possible form by taking real single crystals instead of pseudo-single crystalline aggregates originally used and plastic-ally stretching the material by a few percents instead of rolling it out. When studied in this way the anisotropy phenomena are found to occur regardless of the direction in which the single crystal is stretched, the direction of minimum magnetic
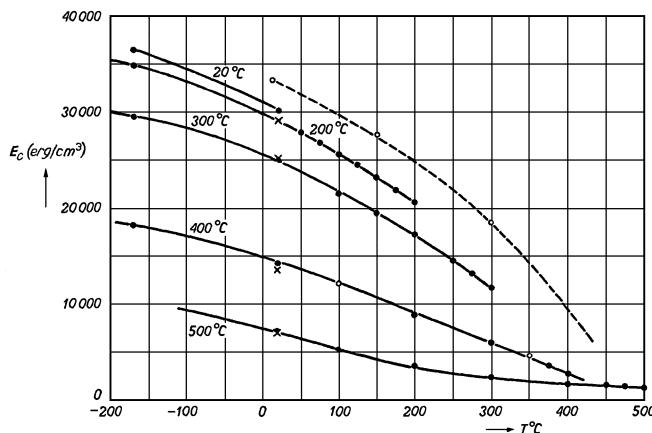
Fig. 10.

E_A vs T for a pseudo-unicrystalline strip of cold rolled nickel iron annealed at 500 ° C. Dotted line: anistropy of completely annealed single crystals.

energy always lying normal to the direction of stretch and in the surface of the strip.

The analogy with Fe_3O_4 at low temperatures is unmistak-able. Here as there the crystal lattice has a higher symmetry than the magnetic anisotropy. Here as there an ordered arrange-ment may be taken as the cause of the phenomena observed. It will be remembered, that in the nickel iron alloys showing the effect the ions tend to an ordering of the type AB_3.

Our experiences with Fe_3O_4 make us hesitate however to consider an ordered arrangement of the nickel and iron atoms to be the cause of the anisotropy phenomena. It might just as well be that the 3 d-electrons play some unexpected role in this second problem also

After the completion of the investigation by RATHENAU, DIJKSTRA has made another experiment on the "fernicubes"

("fernicube" is the trade name under which the cold-rolled nickel iron alloys serving as cores for loading coils are brought on the market,) which is perhaps worth while recording here.

The dependence of the crystal anisotropy and the stress anisotropy on the temperature is very different, as is well known. It seemed to be of interest also to study the dependence upon temperature of the anisotropy due to plastic deformation. The strip had of course first to be annealed at a temperature lying above the temperature interval to be studied, but so low as to not destroy the anisotropy completely. The temperature dependence of the remaining anisotropy was determined after annealing had been carried out at various temperatures ranging from 20 to $500°$C. It proved to be of the same type as is found for the crystal anisotropy (Fig. 10). The interpretation of this result must wait further developments in this field.

§ 10. SOME CONSIDERATIONS ON ALLOYS OF HIGH MAGNETIC STRENGTH

It has often been remarked, that the internal stresses calculated for an alloy like Fe_2NiAl when based upon the magnetostrictive properties alone are extremely high. The KERSTEN theory of the coercive force, which takes into account the effect of unmagnetic inclusions, does not make this situation seem more hopeful, because a primary necessity for obtaining magnetic strength in any alloy always remains a strong anisotropy. It is suggested therefore that in alloys of the $Fe\,Ni\,Al$ type and related ones, a kind of „chemical" anisotropy lies at the root of the observed magnetic strength rather than the ordinary stress anisotropy. Age hardening experiments on many other alloys have sufficiently shown that what happens in a super-cooled alloy on annealing may differ considerably from the simple picture of two components A and B separating from a homogeneous mixture. Structural details often play a decisive role. We shall return to this matter in Chapter III p. 68.

II. DYNAMICS OF FERROMAGNETISM

We are now about to discuss the effect that variations in the rate of change of the magnetic field may have on the process of magnetization. According to the second induction law each change of magnetic flux is accompanied by an e.m.f. along a path surrounding this flux.

In metals the eddy currents set up as a result of this e.m.f. will have a considerable influence upon the process of magnetization as soon as the quantity

$$\delta = \frac{c}{\sqrt{2\pi\sigma\omega\mu}} \tag{14}$$

assumes values equal to or smaller than the minimum dimensions of the specimen in a plane normal to the direction of magnetization. (In (14) c denotes the velocity of light, σ the conductivity, ω the circular frequency and μ the permeability). If such is the case the specimen is said to show *magnetic skin effect*, the magnetic flux being concentrated in a layer of effective thickness δ below the surface.

The distribution as to phase and amplitude of the magnetic flux and consequently the amount of heat developed in the ferromagnet as a result of the eddy currents have been calculated for straight cylinders of infinite length [1]. The results for this particular form of specimens can be expressed in the following rules:

a. Immediately below the surface of the cylinder there is no

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[1] K. L. Scott, *Proc. Inst. Radio Engineers*, **18** (1930) 1750: *Bell Syst. Techn. Publ.* B 620.

time lag between the induction and the (external) field.
The internal field is moreover equal to the external field.

b. If at a given moment a constant internal field is applied
to the sample, the induction B at some distance below
the surface will increase only with a certain time lag, but
the final value of B is reached asymptotically throughout
the sample without any oscillations. The form of the
hysteresis loop will therefore be determined correctly,
provided the time lag is short with respect to the free
period of the ballistic galvanometer.

c. The formula for the amount of heat developed per. cm^2
of the surface, at frequencies high enough to cause δ to be
small in respect of the diameter of the cylinder, may be
adequately written as follows:

$$W = \frac{1}{8\pi} \cdot \mu H_e^2 \cdot \delta. \tag{15}$$

In this expression $\frac{1}{8\pi}\mu \cdot H_e^2 = \frac{H_e \cdot I_0}{2}$ denotes the mean

magnetic energy at the surface of the cylinder; δ as already
mentioned denotes the depth to which the field and the
induction effectively penetrate. Remembering that δ varies
as $\mu^{-\frac{1}{2}}$, the variation of W with μ for high frequencies evi-
dently is of the form

$$W = C \cdot \mu^{+\frac{1}{2}}, \tag{16}$$

the effect of the increasing flux overbalancing the effect
of the decreasing thickness of the surface layer.

*The above rules break down for ferromagnetic specimens with
appreciable demagnetization.* As a result of the breakdown of
rule b, measurements of the hysteresis by means of a ballistic
galvanometer on ferromagnetic bars or ellipsoids may lead to
quite erroneous results, if no suitable precautions are taken
to make the variation of the field sufficiently slow. (Cf. SNOEK,
Physica, 8 (1941) 426, reprinted at the end of this book,
Appendix II).

§ 12. MAGNETIC SKIN EFFECT OF A FERROMAGNETIC SPHERE

There are further interesting consequences for the heating of ferromagnetic bodies in a h.f. coil, this heating process showing quite interesting anomalies in the neighbourhood of the Curie point.

The peculiar situation arising when magnetic skin effect occurs in a ferromagnetic body with appreciable demagnetization, is most easily demonstrated in the case of a sphere.

Formulae for this case have been kindly derived at my request by C. J. BOUWKAMP and D. POLDER of this laboratory. It afterwards came to our knowledge that the same problem had already been solved by M. DIVILKOVSKY. The results of this author being identical with those obtained by BOUWKAMP and POLDER, we refer for a detailed account of these calculations to DIVILKOVSKY's paper [1]. Here we shall only use the final results and analyse them, so as to show the physical background of the phenomena. Let $\alpha = \dfrac{R}{\delta}$ be the ratio of the radius of the sphere to the effective thickness of the magnetic layer and H_0 the amplitude of the magnetic field varying with the (circular) frequency ω. The total amount of heat developed in the sphere is given by DIVILKOVSKY in the following form:

$$W = H_0^2 \cdot \frac{R^3 \omega}{4} \cdot \frac{3\mu}{2\alpha^2} \cdot \frac{\alpha - 1}{1 + \dfrac{\mu - 1}{\alpha} + \dfrac{(\mu - 1)^2}{2\alpha^2}\left(1 - \dfrac{1}{\alpha} + \dfrac{1}{\alpha^2}\right)} \quad (17)$$

This result may be considerably simplified if we assume $\mu \gg 1$ and $\alpha = \dfrac{R}{\delta} \gg 1$. Introducing the new quantity

$$p = \frac{\mu}{2\alpha} = \frac{\mu\delta}{2R} \tag{18}$$

[1] M. DIVILKOVSKY, Le problème d'une sphère métallique dans un champ magnétique alternatif homogène et son application à la théorie des fours à induction, *Journal of Physics Moscow*, 1° (1939) 471.

it is easily shown that (17) can be written in the simple form

$$W = \frac{3}{4} \cdot H_0^2 \cdot R^3 \cdot \omega \cdot \cfrac{1}{\cfrac{2}{p} + 2 + p} \, . \qquad (19)$$

Equation (19) has a maximum near $p = 1$. For $p \ll 1$ and $p \gg 1$ it varies as p^{+1} and p^{-1} respectively.

p on the other hand contains the factor $\mu \cdot \delta$ also found in (15) and is proportional to $\mu^{+\frac{1}{2}}$

It thus follows that under certain conditions the dependence of W on μ may be the same as in the case of the infinitely
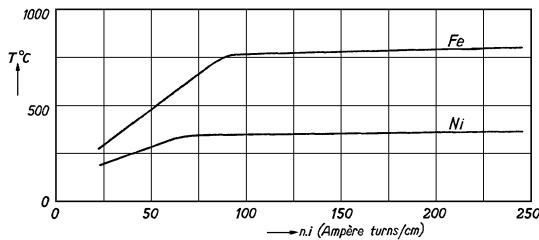
Fig. 11.

Equilibrium temperatures of iron and nickel wires heated in a h.f. magnetic field (wavelength about 800 meter). At the Curie temperature the increase in temperature with increasing current in the h.f. coil temporarily stops due to the strong decrease in μ, the heat developed varying as $\mu^{-\frac{1}{2}}$ in this case.

long cylinder, but that also the exponent may change sign, the condition for this to occur being

$$p = \frac{\mu \cdot \delta}{2R} \cdot \gg 1 \, . \qquad (20)$$

It is to be remembered that δ/R is supposed to be smaller than one, so that in order that (20) shall be true the value of μ must be fairly high, e.g., a hundred or more.

In a ferromagnet a maximum in the value of the initial permeability is encountered immediately below the Curie temperature (Cf. § 7) followed by a sudden drop towards unity, when that temperature is reached. At medium field strength

the maximum is less obvious, but the sudden drop towards lower values near the Curie temperature remains.

This sudden drop in the permeability will have different consequences for the h.f. heating of ferromagnetic bodies of various forms. In long and thin specimens which are magnetized in the direction of their greatest dimension, the heat will vary as $\mu^{+\frac{1}{2}}$. Consequently the curve giving the variation of the temperature with the current in the coil is more or less flattened in the neighbourhood of the Curie temperature (c.f. Fig. 11). In experiments on iron plates magnetized in a direction normal
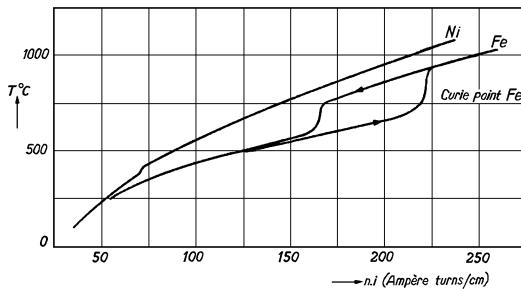
Fig. 12.
Same as Fig. 11, but now the specimens are flat plates magnetized in a direction normal to the field. The retarded „jump" in the temperature observed for iron, is due to the heat developed varying as $\mu^{-\frac{1}{2}}$ and is explained in Fig. 14.

to the surface an interesting phenomenon of temperature hysteresis was found to occur (Fig. 12). At a certain value of the slowly rising h.f. current the temperature suddenly rises by several hundreds of degrees. The explanation lies in the fact that the drop in μ_0 in this case leads to a sudden increase in the amount of heat developed. The temperature hysteresis shown in Fig. 11 may be illustrated visually very easily by the following experiment:

An iron wire of 1 mm diameter is bent into the form illustrated in Fig. 13 and then slowly moved into the interior of a h.f. coil. At a certain critical distance the colour of the iron wire, which is initially a dull red, suddenly flares up to a brilliant white. On increasing the distance from the wire to

the coil the high temperature is retained over a considerable distance, after which a sudden drop to a dull red again occurs.
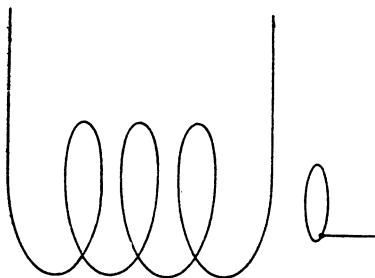
Fig. 13.

Experimental arrangement demonstrating visually the sudden increase in temperature with increasing H. The iron specimen is slowly moved in and out the h.f. coil.

The way in which such a temperature hysteresis as represented in Fig. 12 arises, is indicated more fully by the schematic representation of Fig. 14.

In this figure the logarithms of the energies absorbed and given off have been plotted against the logarithm of the absolute temperature. Assuming for simplicity that energy is given off only by radiation, the curve for the energy lost by the specimen is a straight line cutting the T-axis at an angle, the tangent of which is equal to four or five depending on the nature of the surface.

As to the dissipated power this quantity varies with the temperature mainly as a result of variations of μ. The relatively slight variations due to changes in the resistance need not be taken into account.

Again for reasons of simplicity the value of μ is supposed to be equal to e.g. a hundred below the Curie temperature, and equal to unity above this temperature.

We may then plot two horizontal lines, which for a given value of the h.f. current give the power absorbed, depending on whether the value of μ_0 is equal to hundred or to one. In the situation represented

Fig. 14.

Energy balance in a short ferromagnetic specimen heated in a h.f. magnetic field.

by Fig. 14, in which the lower line cuts the curve for the radiated energy at a point below the Curie temperature,

there are obviously two points of stable equilibrium.

On varying the h.f. current the position of the horizontal lines is displaced with respect to the curve representing the energy given off and the reader can easily imagine how curves of the shape as those represented in Fig. 12 come about.

The physical background of the mathematical condition $p \gg 1$, which marks the change from $\mu^{+\frac{1}{2}}$ to $\mu^{-\frac{1}{2}}$, remains to be discussed.

To that end we must return to equation (15), which as will be remembered gives in a condensed form the expression for the heat developed per cm^2 in an infinitely long cylinder.

As remarked before, the value $+\frac{1}{2}$ of the exponent of μ is the result of the influence of the increased induction over-balancing the effect of the decreasing thickness of the surface layer.

In bodies with a strong demagnetization the relation

$$B = \mu \cdot H_e \qquad (21)$$

between the induction B and the exciting field H_e, as is well known no longer holds, but has to be replaced by

$$B = \mu' \cdot H_e, \qquad (22)$$

where μ' depends mainly on the form of the specimen, the value of μ being without much influence on μ' if $\mu \gg \mu'$.

From equations for the magnetic sphere it can be seen (c.f. DIVILKOVSKY) that under all circumstances the distribution of the poles on the surface of the sphere is the same as if it were magnetized in a constant field. On the other hand the total strength of these poles producing the demagnetizing field is always proportional to the total magnetic flux passing through the equator of this sphere. It is useful therefore to write the relation between the internal field H_i and the external field H_e in a form in which this flux φ makes its appearance.

In the case of static magnetization we have between H_i and H_e the relation

$$H_i = H_e - D.B, \qquad (23)$$

where D is the demagnetizing factor (equal to $\frac{1}{3}$ for a sphere).

Substituting $H_i = \dfrac{1}{\mu} B$ into (23) we find that the condition that the value of μ shall be without much effect on the induction is given by $\dfrac{1}{\mu} \ll D$ or

$$\mu \cdot D \gg 1, \tag{24}$$

For high frequencies we write (23) in the form

$$H_i = H_e - \frac{D}{\pi R_e^2} \cdot \varphi \tag{25}$$

where φ is the magnetic flux and R_e is the radius of the specimen both measured along the equator. We may further assume that φ is restricted wholly to an area equal to $2\pi R_e \cdot \delta$, (where δ as before denotes the effective thickness of the magnetized layer). We thus find

$$\frac{1}{\mu} B = H_i = H_e - \frac{D}{\pi R_e^2} \cdot 2\pi R_e \cdot \delta \cdot B \tag{26}$$

and the condition that μ shall be without much effect on the value of the flux develops into

$$2 \frac{\mu \cdot D \cdot \delta}{R_e} \gg 1, \tag{27}$$

which for the sphere specializes to

$$p = \tfrac{2}{3} \frac{\mu \cdot \delta}{R_e} \gg 1 \text{ which is practically identical with (20)}$$

We thus see: a) that the combined occurrence of μ and $\dfrac{\delta}{R}$ in p is a direct consequence of the skin effect pressing the demagnetizing φ into a narrow ring of thickness δ; b) that the transition from the proportionality with $\mu^{+\frac{1}{2}}$ to a proportionality with $\mu^{-\frac{1}{2}}$ is due to the fact that H_i no longer equals H_e if μ takes on high values.

§ 13. AFTER-EFFECT

If, as a result of some retarding mechanism other than eddy currents, a phase angle is found to exist between B and H throughout the material, we are justified in calling it "after-effect". By way of introduction we will first point out some very general features, which are found in all phenomena of after-effect. Suppose we have a linear system acted upon by an external "force" X. We take X equal to

$$X = X_0 e^{i\omega t} \tag{28}$$

and expect to find for the resulting displacement Y

$$Y = Y_0 e^{i\omega t} \tag{29}$$

Between Y_0 and X_0 a relation exists of the form

$$Y_0 = \varepsilon(\omega) X_0 \tag{30}$$

where ε is a constant for variations in the amplitudes X_0 and Y_0 of the force and the resulting displacement respectively, but may depend on ω. The function $\varepsilon(\omega)$ may be complex and energy is dissipated at frequencies for which this is the case.

If for instance the object to be studied is a dielectric, X is the electric field E and Y the displacement D, while ε is the dielectric constant. Between the real part of $\varepsilon(\omega)$ and the imaginary part certain well-known mathematical relations exist [1], which are of such a form as to make the knowledge of one of them for all values of ω sufficient to know the other also.

From a mathematical as well as from a physical standpoint the most simple case is met when the after-effect takes on the form

$$\varepsilon = \varepsilon_0 + \frac{\varepsilon_1}{1 + j\omega\tau} \tag{31}$$

where $\varepsilon_0 + \varepsilon_1$ represents the value of the dielectric constant for static measurements and ε_0 the value obtained for fre-

[1] H. A. KRAMERS, *Atti Congr. Fis. Como* (1927) 547; F. BRONS, diss. Groningen 1938 p. 8.

quencies $\omega \gg \dfrac{1}{\tau}$; τ is called the relaxation time. If $\varepsilon_1 \ll \varepsilon_0$, advantage may lie in the measurement of the loss angle

$$\tan \delta = \frac{\varepsilon_1}{\varepsilon_0} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2}. \tag{32}$$

Just as complete an insight into the phenomenon is gained however by studying the variation of the real part of ε with frequency given by

$$\varepsilon_r = \varepsilon_0 + \varepsilon_1 \cdot \frac{1}{1 + \omega^2\,\tau^2} \tag{33}$$

Often it is found impossible to investigate the whole range of frequencies containing values of ω for which $\omega\tau \ll 1$ as well as $\omega\tau \gg 1$, due to experimental difficulties, which will however not be discussed here.

Instead of this we will inquire into the possible causes of after-effect. Now fortunately it can be said, that notwithstanding the fact that after-effect may present itself under innumerably varied forms and may be the result of very different causes, trivial as well as deeply founded ones, there nevertheless exist some general points of view which are valid for all phenomena of after-effect.

From experience in various branches of physics (dielectrics, para- and ferromagnetism, elasticity, acoustics) [1] it has become increasingly evident that after-effects are always due to the retarded restoration of a thermodynamic equilibrium, which has been thrown out of balance by the action of the external force X. Such a recovery is in general only possible through a process of diffusion of matter or energy [2]. The relaxation time τ, characteristic of the after-effect really is the time required by the diffusion process to restore the equilibrium.

If more than one value of τ is required to give an adequate

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[1] R. DE L. KRONIG, *Z. techn. Phys.*, **19** (1938) 509; J. L. SNOEK AND F. K. DU PRÉ, *Philips Techn. Rev.*, **8** (1946) 57.

[2] The word "diffusion" is used here in a slightly more general sense than usual.

description of the after effect, it is not necessary to assume that as many different mechanisms of diffusion are involved, as there are values of τ. For diffusion the general relation holds

$$\overline{\Delta x^2} = 2\,Dt$$

where $\overline{\Delta x^2}$ denotes the average distance covered by the diffusing particles (or energy), D the coefficient of diffusion, t the time.

Variations in the value of τ may be caused by variations in $\overline{\Delta x^2}$ as well as by variations of D, and it is not possible beforehand to decide between these possibilities. These variations on the other hand may be the result of some secondary structure in the material.

The above rule being accepted — and there is little reason to doubt its general validity — it follows conversely, that the study of after-effect informs us about the properties of the diffusion mechanisms involved and thus may contribute to a better understanding of what is going on inside a solid.

The *magnitude* of the effect (by this we mean the ratio $\varepsilon_1/\varepsilon_0$) in many cases provides a first indication of the relative importance of the diffusion process involved for the phenomenon we are studying. When $\varepsilon_1 \ll \varepsilon_0$, there is usually only a very loose connection between the after-effect and the diffusion process. As an example we take the thermo-elastic effect studied by ZENER [1]: it is known that substances having a positive (or negative) coefficient of expansion become warmer (resp. cooler) on compression. If in the course of a cycle an appreciable interchange of heat with the surroundings takes place, an after-effect is the result. It is well known that the prevention of such an interchange does not influence the elastic constant to a great extent. Therefore the loss angles involved with elastic after-effect due to thermal currents will in general not be large.

Larger loss angles are to be expected, if the diffusion affects the whole phenomenon, as is e.g. sometimes the case with

[1] C. ZENER, *Phys. Rev.*, **52** (1937) 230; **53** (1938) 90.

paramagnetism. Large phase angles between the force X and the displacement Y are consequently found here, provided this angle is defined in the right way. If δ were defined as the angle between B and H it would be very small in the case of paramagnetism. This is fully explained by the fact, that the contribution of the paramagnetic substance to the magnetic displacement is only small when compared to the contribution made by the vacuum. The latter of course is unaffected by after-effect. If on the other hand δ denotes the angle between I and H, large angles may be found in paramagnetics in those frequency regions, where the diffusion process, which is essential for the establishment of magnetic equilibrium, is affected.

We have seen, that the quantity $\varepsilon_1/\varepsilon_0$ informs us about the relative importance of the after-effect for the phenomenon we are studying, while τ informs us about the velocity of the diffusion process. If nothing more is known, we know very little yet about the physical cause of the after-effect. To get further we shall have to try our luck and make an atomic picture, which seems to meet the case well. An analysis of the influence of temperature and of the chemical composition on the phenomenon will take us a long way towards solving the problem, but more often will not supply us with the necessary information.

Fortunately there is still another point of view, which may prove useful. In general diffusion is only possible for

> *a.* heat
> *b.* ions (or atoms)
> *c.* electrons

Of *a*) we have seen an example in the thermo-elastic effect. On *b*) we will dwell while dealing with the effect of carbon and nitrogen on the magnetic properties of iron.

After-effect due to electrons has hitherto been found only in studying paramagnetism and acoustics. In this volume we will show that certain after-effects found in ferromagnetic metals as well as in non-metals probably must be ascribed to the diffusion of electrons.

Apart from the newly discovered particles, which are important in nuclear physics, no other possibilities seem to present themselves. We therefore are justified in dividing the after-effects into three groups, which may be named *thermic*, *ionic*, and *electronic* after-effects respectively.

§ 14. DISACCOMODATION (D.A.)

The phenomenon of disaccomodation (occasionally shortened to D.A. in the following) was studied by C. E. WEBB and L. H. FORD in a brilliant paper [1], which we recommend studying.

It was called by them *time decrease of permeability* in order to stress what they thought to be the main feature of the phenomenon, a gradual and seemingly spontaneous decline of the initial permeability in the course of time.

In this respect the phenomenon obviously strongly resembles the phenomenon of aging in iron and steel, which really is one of the oldest known cases of precipitation hardening.

The French using the term „vieilissement réversible" or "reversible aging" want to express at the same time the fundamental difference existing between D.A. and other aging phenomena, namely that the effect can be reproduced at will merely by subjecting the material anew to a magnetic (or mechanical) shock.

The magnetic field itself being the cause of an inner disturbance in the material, it will be clear at once, that a study of the phenomenon is best made by measurements of the initial permeability μ_0.

For a "magnetic shock" the best treatment to be chosen obviously is a treatment by which no polarity is left in the material. This can best be accomplished by subjecting the material to an alternating field, which initially should be sufficiently strong to produce magnetic saturation and then is allowed to decline gradually towards zero.

After the demagnetizing treatment a determination of μ_0 should of course take place as soon as possible. As a rule this quantity when measured by means of a small alternating

[1] C. E. WEBB AND L. H. FORD, *J. Inst. el. Eng.*, **75** (1934) 787.

current is found to change very rapidly with time, so that a determination of the true "initial" value of the initial permeability is a matter of some difficulty.

If the demagnetizing treatment is carried out well, the curves indicating the variation of μ_0 with time prove to have the same shape regardless of any previous magnetic treatment, and the term "reversible aging", apart from the paradox hiding in it, thus seems not wholly out of place.

As shown in a formal theory developed by us in 1938 [1], D.A. must be expected to occur only in substances which are spontaneously polarized, and there it should be always accompanied by magnetic after-effect (M.A.) at practically the same rate of change with time. D.A. represents only a very special aspect of after-effect in materials having a complicated secondary structure.

The fundamental fact underlying D.A. evidently is, that the situation $B = 0$, $H = 0$ aimed at each time by the demagnetizing treatment, represents no well defined state, the division of the ferromagnetic material into "domains" separated by "Bloch zones" being possible in a number of different ways.

In their newly found positions the Bloch zones or the domains as a whole evidently find some means at hand to adapt themselves gradually to their new conditions.

In the special case of iron containing some carbon or nitrogen in solid solution it is even possible to specify very clearly the way in which this adaptation takes place. This has not yet proved possible for another case of D.A. found by us to occur in certain ferromagnetic non-metals, which will be described in § 17.

§ 15. DISACCOMODATION AND MAGNETIC AFTER-EFFECT IN α-IRON (IONIC AFTER-EFFECT)

In *Physica* 1938 we have deduced from certain characteristic features of the phenomenon of D.A. a formal theory explaining

[1] J. L. SNOEK, *Physica*, 's-Grav. 5 (1938) 663.

the latter in terms of magnetic after-effect. The Bloch zones are supposed to develop certain potential minima at the place where they have been resting for a sufficiently long time, and thus it becomes increasingly difficult to make them move in a lateral direction.

So far the theory is very general and very formal. In the same paper however a more special hypothesis was made on the nature of these potential minima. It was suggested that the magnetostrictive stresses in a material showing elastic after-effect were responsible for the formation of these local potential minima.

The fact that the samples of α-iron under discussion (by α-iron we mean iron alloys having a cubic body centered lattice) show indeed elastic after-effect and that the magnetic after-effect is absent in samples not showing the elastic effect, of course already by itself lends a strong support to such a hypothesis.

To our suggestions the objection has been made that the magnitude of the magnetic effect surpasses the magnitude of the elastic effect several times [1].

To this objection the answer is that our calculations made in 1938 already allowed for a magnetic after-effect, which may in principle be made arbitrarily strong as compared to the elastic after-effect.

At that time however it was not yet clear what is the main factor determining the static value of μ_0 in α-iron.

According to more recent views unmagnetic inclusions must be held mainly responsible for keeping the initial permeability of α-iron down.

It is the object of this note to calculate the ratio of the magnetic after-effect to the elastic after-effect from the value of the coercive force, assuming that the hysteresis in α-iron is wholly of the inclusion type.

We have quite generally

$$\frac{dI}{dH} = \frac{dI}{dx} : \frac{dH}{dx}, \tag{34}$$

[1] B. and D., p. 267; Grundlagen, p. 81.

in which x denotes the displacement of a Bloch zone. In this expression the quantity $\dfrac{\mathrm{d}I}{\mathrm{d}x}$ is an immaterial constant but $\dfrac{\mathrm{d}H}{\mathrm{d}x}$ is to be calculated in its dependence on various factors.

According to general theory [1] formulated by M. KERSTEN we have

$$H = \frac{1}{2I_{\max}} \cdot \left(\frac{\gamma}{O} \cdot \frac{\mathrm{d}O}{\mathrm{d}x} + \frac{\mathrm{d}\gamma}{\mathrm{d}x} \right) \tag{35}$$

where γ as before denotes the intrinsic energy of a Bloch zone, O the active surface and $I_{\max}$ the saturation value of the magnetization.

We write γ as the sum of two terms, γ_1 and γ_2 $(= \gamma_m f(x))$

$$\gamma = \gamma_1 + \gamma_2 = 2\, E_c \cdot \delta + \tfrac{1}{2} \cdot \lambda^2 E \cdot \delta f(x) \tag{36}$$

where γ_1 represents the anisotropy energy and γ_2 the magnetostrictive energy; the value of $f(x)$ is very near to 1.

Assuming $E_c = 1.4 \times 10^5$ erg/cm³, the Young modulus $E = 2 \times 10^{12}$ dyn/cm², the magnetostriction $\lambda = 1.8 \times 10^{-6}$, values all holding for pure iron, we find for the ratio from γ_2 to γ_1

$$\frac{\gamma_2}{\gamma_1} \sim \frac{\gamma_m}{\gamma_1} = \frac{\tfrac{1}{2} \cdot \lambda^2 \cdot E}{2E_c} = \frac{324}{280} \cdot 10^{-3} \sim 0.001 \ . \tag{37}$$

This result might induce us to imagine that γ_2 is wholly unimportant with respect to γ_1. For γ itself this is true. However in $\dfrac{\mathrm{d}\gamma}{\mathrm{d}x}$ the term $\dfrac{\mathrm{d}\gamma_2}{\mathrm{d}x}$ provides the main contribution, $\dfrac{\mathrm{d}\gamma_1}{\mathrm{d}x}$ being zero.

We thus are led to simplify (35) to

$$H = \frac{1}{2I_{\max}} \cdot \left(\frac{\gamma_1}{O} \cdot \frac{\mathrm{d}O}{\mathrm{d}x} + \frac{\mathrm{d}\gamma_2}{\mathrm{d}x} \right) \tag{38}$$

The inclusion model leads to the expression

[1] M. KERSTEN, *Phys. Z.*, **44** (1943) 63.

$$\frac{1}{O} \cdot \frac{\mathrm{d}O}{\mathrm{d}x} = 2\pi \frac{x}{s^2}, \tag{39}$$

s denoting the distance between neighbouring inclusions.

If c is the magnitude of the elastic after-effect, then it can easily be shown that $c\gamma_m$ is the total amount of energy lost per cm^2 in the Bloch zone as a result of the adaptation of the magnetostrictive stresses by means of elastic after-effect.

In order to calculate $\dfrac{\mathrm{d}\gamma_2}{\mathrm{d}x}$ as a function of x, it is necessary to make some assumptions about the form and the width of the potential minimum created by the elastic after-effect. We shall assume that the potential is a quadratic function of x and that it has retained its normal value, as soon as the Bloch zone is displaced over a distance equal to δ. We then may write

$$\gamma_2(x) = c \cdot \left(\frac{x}{\delta}\right)^2 \cdot \gamma_m + (1 - c)\gamma_m \tag{40}$$

from which follows for H:

$$H = \frac{x}{2I_{\max}} \cdot \left(\frac{2\pi}{s^2} \cdot \gamma_1 + \frac{2c}{\delta^2} \cdot \gamma_m\right) \tag{41}$$

and for $\dfrac{\mathrm{d}H}{\mathrm{d}x}$:

$$\frac{\mathrm{d}H}{\mathrm{d}x} = \frac{\pi\,\gamma_1}{I_{\max}\,s^2} \cdot \left(1 + \frac{s^2}{\delta^2} \cdot \frac{c}{\pi} \cdot \frac{\gamma_m}{\gamma_1}\right) = \frac{\pi\,\gamma_1}{I_{\max}\,s^2}(1 + C). \tag{42}$$

The magnitude of the second term between brackets decides the magnitude of the magnetic after-effect. For the ratio R between the magnetic and the elastic effect we find

$$R = \frac{C}{c} = \frac{1}{\pi} \cdot \left(\frac{s}{\delta}\right)^2 \cdot \frac{\gamma_m}{\gamma_1}. \tag{43}$$

From the fact, that $s \ll \delta$ we see at once that this ratio may be larger than unity, notwithstanding the fact that $\dfrac{\gamma_2}{\gamma_1}$

is not larger than 0.001. In order to calculate R it is advisable to substitute in (43) the formula for the coercive force H_c

$$H_c = \frac{\pi}{2} \cdot \frac{\gamma_1}{I_{max}} \cdot \frac{d}{s^2}$$

which leads to

$$R = \frac{d}{\delta} \cdot \frac{\lambda^2 E}{4 H_c . I}. \qquad (44)$$

The coercive force of the iron used by us being equal to about 0.1 Oersted we find for R:

$$R = \frac{d}{\delta} \cdot \frac{648}{680} \sim \frac{d}{\delta} \sim 20 * \qquad (45)$$

and thus we are led to a value for R greatly exceeding unity. To this it may be added that the value of λ used in deriving (45) is the one valid for the (100) direction. In other directions very much larger values occur. Inside a Bloch zone we probably have to do with a mean between all these values.

The conclusion is that the magnetic after-effect in a very pure iron may indeed exceed the elastic effect by a large factor and that the cause of this is the relatively large energy gradient set up in the immediate neighbourhood of the Bloch zone due to this comparatively narrow zone "digging itself in".

§ 16. ELASTIC AFTER EFFECT IN α-IRON

Ever since our discovery that minute amounts of either carbon or nitrogen are capable of producing elastic and magnetic after effect in the iron lattice, the closer study of the elastic effect has been demanding our attention [1].

In 1942 a detailed theory of the effect was developed by us, leading to interesting consequences, which can be tested by experiment.

* *Phys. Z.*, **44** (1943) 73, Fig. 4.
[1] J. L. SNOEK, *Physica*, 6 (1939) 161, 321, 591, 797; 8 (1941) 711; *Ned. Tijdschr. v. Natuurk.*, **7** (1940) 133; 8 (1941) 177; *Physica*, 9 (1942) 862; *Chemisch Weekblad*, **39** (1942) 1.

The absolute magnitude of the effect for carbon could be related to the cell dimensions of tetragonal martensite in a very simple way. An experimental test of this relationship has been carried out by DIJKSTRA. He was also able to verify our prediction that in the (111) direction the effect would be found to be zero.

For his quantitative determination of the relation between the elastic after-effect and the concentration of the carbon or nitrogen atoms DIJKSTRA had no direct means of measuring this concentration at his disposal.

He had therefore to make use of measurements of the increase in the specific electric resistance ϱ as a means of determining the number of solved atoms present.

The constant relating this increase $\varDelta\varrho$ to the concentration was determined separately on polycrystalline specimens having a more suitable weight and form.

Before describing DIJKSTRA's experiments and results we will give a short account of the theory developed during the war. A more rigourous mathematical treatment has been given by POLDER (cf. Appendix IV).

Geometrical considerations have led crystallographers to suggest as possible locations for the C-atom in the cubic body centered lattice of iron the following positions (Fig. 15)

$(\frac{1}{2}, 0, 0)$ $(0, \frac{1}{2}, \frac{1}{2})$ (x-positions)

$(0, \frac{1}{2}, 0)$ $(\frac{1}{2}, 0, \frac{1}{2})$ (y-positions)

$(0, 0, \frac{1}{2})$ $(\frac{1}{2}, \frac{1}{2}, 0)$ (z-positions)

Identifying the x-axis of an orthogonal system of axes with the (100) direction, y with (010), z with (001), it is seen that atoms in x-positions lie midway between iron atoms connected by a line along (100), causing these atoms to be separated from each other slightly more than the other neighbouring atoms. Likewise the occupation
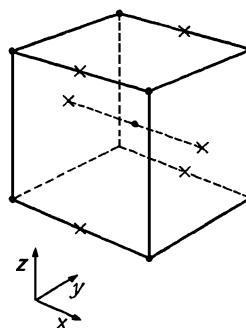

Fig. 15.
Possible locations of C and N (H) atoms in the lattice of α iron (x-positions).

of y-positions causes the lattice to expand preferentially in the direction of the y-axis, while z-positions do the same for the z-axis.

As there are in total three times as many x-, y- and z-positions as iron atoms, while the molar concentration of the carbon does not greatly exceed 1%, of course only a very small fraction of the available positions will be occupied.

In the absence of any external forces and assuming that at room temperature diffusion is still possible to a limited extent, it is natural to suppose, that in the mean equal numbers of the x, y and z positions will be occupied, the lattice thus remaining in the mean cubic. The explanation of the after-effect now is, that if an elastic pull is exerted along one of these axes, the distribution of C-atoms over the x, y and z-positions is changed, so as to favour an extension in this direction.

Following purely thermodynamic lines the calculation of the effect along the $[100]$ axis may run as follows: if λ_1 is the elastic part of the (longitudinal) deformation, λ_2 the part due to the excess of C-atoms on x-positions found there after due time, we have

$$\lambda_1 = -\frac{p}{E}, \tag{46}$$

$$\lambda_2 = \frac{\partial \lambda}{\partial \Delta c} \cdot \Delta c, \tag{47}$$

where p is the pressure and Δc the excess (molar) concentration of the occupied x-positions over the y or z-positions. As we shall show later on, the constant $\dfrac{\partial \lambda}{\partial \Delta c}$ in equation (47) can be calculated from the cell dimensions of tetragonal martensite and is found to be equal to 0.58:

$$\frac{\partial \lambda}{\partial \Delta c} = 0.58 \tag{48}[1]$$

[1] Later observations by K. HONDA AND N. NISHIYAMA, *Sci. Rep. Toh. Univ.*, **21** (1932) 299 and by G. HÄGG, *Stahl u. Eisen*, **54** (1934) 1328, lead to a somewhat higher value for $\dfrac{\partial \lambda}{\partial \Delta c}$ making the agreement between theory and experiment better than before.

The entropy S per mol depends on the molar concentrations c_x, c_y, c_z of C-atoms located on the x, y and z positions respectively; hence:

$$- S = R\,(c_x \ln c_x + c_y \ln c_y + c_z \ln c_z). \qquad (49)$$

An excess $\varDelta\,c$ in the molar concentration of x-positions arises by putting

$$c_x = c_0 + \tfrac{2}{3}\,\varDelta\,c \qquad\qquad c_y = c_z = c_0 - \tfrac{1}{3}\,\varDelta\,c \qquad (50)$$

(c_0 is equal to one third of the molar concentration of the carbon atoms). Developing S into a Taylor series we find for $-\varDelta\,S$

$$- \varDelta\,S = \tfrac{1}{3}\cdot(\varDelta\,c)^2 \cdot \frac{\mathrm{d}^2 S}{\mathrm{d}c^2} = \tfrac{1}{3}\cdot(\varDelta\,c)^2 \cdot \frac{R}{c_0}. \qquad (51)$$

Putting V for the molar volume of a gram-atom of iron, we find for the thermodynamic potential per gram-atom

$$\varphi = U - TS + Vp\,(\lambda_1 + \lambda_2) \qquad (52)$$

and require $\dfrac{\partial\varphi}{\partial\,\varDelta\,c}$ to be zero under conditions of final equilibrium.

We find using (49)

$$\frac{\partial\varphi}{\partial\,\varDelta\,c} = \tfrac{2}{3}\cdot\frac{RT}{c_0}\cdot\varDelta\,c + V\cdot p\cdot\frac{\partial\lambda}{\partial\,\varDelta\,c} = 0, \qquad (53)$$

whence follows for $\varDelta\,c$

$$(-?)\ \varDelta\,c = \tfrac{3}{2}\cdot\frac{Vp}{RT}\cdot\frac{\partial\lambda}{\partial\,\varDelta\,c}\cdot c_0 \qquad (54)$$

and

$$\frac{\lambda_2}{\lambda_1} = \tfrac{3}{2}\cdot\frac{E\cdot V}{R\cdot T}\cdot\left(\frac{\partial\lambda}{\partial\,\varDelta\,c}\right)^2\cdot c_0 \qquad (55)$$

Formula (55) gives us the ratio λ_2/λ_1 which may be deduced in several ways from experiment in terms of the molar concentration $C = 3c_0$ and the constant $\dfrac{\partial\lambda}{\partial\,\varDelta\,c}$, which we are now to discuss.

The quantity $\dfrac{\partial \lambda}{\partial \Delta c}$ could be measured, if one succeeded in fixing all C atoms in x-positions and measuring the resulting increase in length in the x-direction. It is highly surprising and
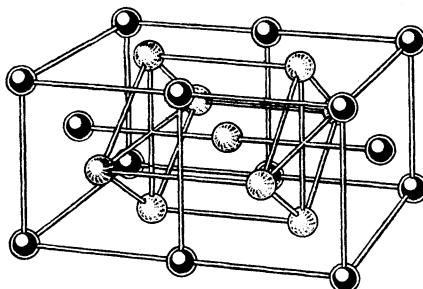
Fig. 16.

Crystallographic model showing the (tetragonally deformed) body centered lattice inside the cubic face centered lattice.

most satisfactory that nature has done so for us in the well-known quenching product: tetragonal martensite. E.C. BAIN and ANGEL St. JOHN have supplied us with a picture of the martensite transformation as early as 1924. [1] As supposed by these authors and afterwards verified by X-ray analysis, the transformation from the γ to the α-state takes place essentially in the way suggested by Fig. 16, where it is shown, that the face centered lattice already contains a body centered lattice extended in one direction by a factor $\sqrt{2}$. By compression along this direction a cubic body centered lattice is formed. The C atoms which in the γ-lattice were lying in the centres and in the middle of the edges of the cubes enter just those positions in, which we have called x, y or z-positions.

Once this has been realized, it is easy to calculate from the data supplied by G. KURDJUMOV and E. KAMINSKY for the cell dimensions of tetragonal
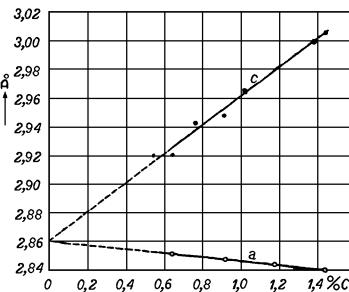
Fig. 17.

Cell dimensions of tetragonal martensite as a function of the carbon content. Measurements by G. KURDJUMOV and E. KAMINSKY. (Z. Phys. **53** (1929) 696.

[1] E. C. BAIN, *Trans. Am. Inst. Min. Met. Engrs*, **70** (1924) 25.

martensite (cf. Fig. 17) the quantity $\dfrac{\partial \lambda}{\partial \Delta c}$, taking for Δc the concentration of the total amount of carbon present.

The experimental determination of $\dfrac{\lambda_2}{\lambda_1}$ was carried out by DIJKSTRA along the same lines as previously indicated by the author: the decrement of a particular form of pendulum, in which the specimen in the form of a small rectangular strip

provided the restoring force, was measured visually for various temperatures. By plotting the result against the temperature (Fig. 18) the effect of carbon is separated from other damping influences.

Fig. 18.

Damping maximum observed in iron containing a few hundredths of a percent of carbon in solid solution.

The height of the maximum is directly proportional to λ_2/λ_1. The specimens were small rectangular strips measuring $50 \times 5 \times 0.15$ mm cut from single crystals prepared following the method of critical stress. The orientation of the crystals was determined approximately by measuring the main loop: the measured height of the remanence immediately tells us whether [111] or [100] is very near to the direction of measurement. In this way it proved possible to lay hands on several specimens having about the above-mentioned orientations. The coercive force of these samples was about 0.15 Oersted, indicating a reasonable magnetic purity.

Loading with nitrogen was done by giving the sample a heat treatment at 600° C for several hours in an atmosphere of hydrogen containing 4% of ammonia. Carbon was introduced by annealing the sample at 700° C in hydrogen which had passed over naphtene.

A first experiment consisted of testing the anisotropy of the effect. Two samples of single crystals were repeatedly "nitrogenized" and "carburized" in the same oven and their after-effect measured.

The sample having a [100] axis nearest to the direction of stress proved to have an after-effect fifteen times stronger than a sample having a [111] axis near to that direction. The effect is therefore clearly anisotropic. Most probably under ideal conditions the effect in the [111] direction would be exactly zero.

Next came the determination of the magnitude λ_2/λ_1 of the effect in the [100] direction as a function of the amount of carbon dissolved in the iron. The only difficulty in these experiments was the determination of the carbon content. Chemical methods being impracticable for such low concentrations as a hundredth of a percent by weight and moreover leading to the destruction of the sample, it was decided to use an indirect method. By suitable arrangements it proved possible to determine the resistance of the samples with an error of less than 0.1 % without damaging the specimen or soldering any contacts on it. The increase in the electric resistance brought about by the addition of carbon could thus be determined with sufficient accuracy to be used as a means of determining the amounts taken up by the specimen.
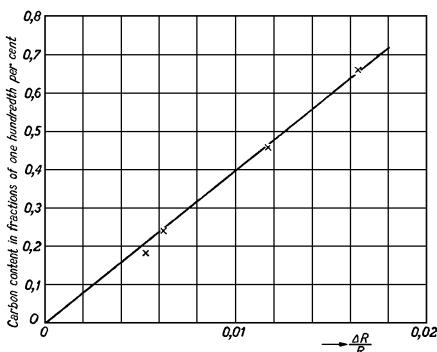
Fig. 19.
Elastic after effect vs increase in electric resistance due to the introduction of carbon in iron (measurements by Dr DIJKSTRA).

Calibration of the electric method was done on a polycrystalline sample of suitable form and weight (a bar weighing 16 gram and having a diameter of 5 mm). By carburizing this bar under constant conditions for a sufficiently long time,

quenching it in oil and carefully determining its increase in weight the amount of carbon taken up could be determined.

Figs. 19 and 20 show that the expected linear relationships between the quantities λ_2/λ_1 and $\dfrac{\varDelta R}{R}$ as well as between $\dfrac{\varDelta R}{R}$ and $\dfrac{\varDelta g}{g}$ are indeed fulfilled. From them we deduce that 0.01%

Fig. 20.

Relative increase in weight vs increase in electric resistance due to the introduction of carbon in iron (measurements by Dr. DIJKSTRA).

by weight of carbon leads to $\dfrac{\varDelta R}{R} = 2.5\%$ and to $\dfrac{\lambda_2}{\lambda_1} = 4.3\%$.

With the aid of equations (48) and (55), one finds $\dfrac{\lambda_2}{\lambda_1} = 3.2\%$.

In Table I we give, besides the above mentioned data on carbon, additional data of the same kind on nitrogenized samples and also some data for polycrystalline samples. The latter are of course subject to some uncertainty due to texture.

TABLE I

Effect of the addition of 0.01% by weight of either C or N on the elastic after-effect and the specific electric resistance of pure iron.

Carbon [100] direction		Carbon polycrystalline		Nitrogen [100] direction	
$\dfrac{\varDelta \lambda}{\lambda}$	$\dfrac{\varDelta R}{R}$	$\dfrac{\varDelta \lambda}{\lambda}$	$\dfrac{\varDelta R}{R}$	$\dfrac{\varDelta \lambda}{\lambda}$	$\dfrac{\varDelta R}{R}$
0.043	0.025	0.015—0.030	0.025	0.032	0.035

§ 17. A NEW TYPE OF D.A. AND M.A. IN FERROMAGNETIC
NON-METALS

Before passing from the low frequency after-effects (l.f. M.A.)
to the high frequency after effects (h.f. M.A.) it is perhaps
worthwhile recording here a newly found case of after effect
and D.A. in non-metals, occupying an intermediate position
between the two classes of phenomena.

Mixed crystals of $Mn\,O\,.\,Fe_2O_3$ and $Zn\,O\,.\,Fe_2O_3$, especially
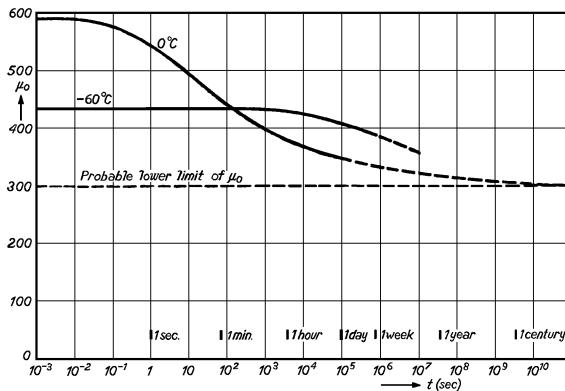
Fig. 21.

μ_0 vs log t as observed on a ferrite at two different temperatures. Here is a case,
where one value of τ clearly does not suffice to describe the variation of μ_0
with time. Note the very long time required to obtain equilibrium conditions
and the very rapid initial changes in μ_0.

those containing some Fe_2O_3 in excess, were found to show
in some cases strong D.A.

Contrary to our findings for α-iron the effect could not
be described by one time of relaxation, appreciable changes
in μ_0 taking place in the second minute after demagnetization
as well as in the second day or month. By demagnetizing with
the aid of a high frequency current and photographically
recording the initial permeability (measured also by means of
a high frequency current) true "initial" values for μ_0 could
be determined with sufficient accuracy, observations being
made within 0.1 second after the beginning of the demagnetizing

treatment. It seems that a state of equilibrium is not reached until after many years. This is shown in Fig. 21, in which μ_0 has been plotted against the logarithm of the time for a ferrite containing 23.5 mols $Mn\ O$, 22.5 mols $Zn\ O$ and 54 mols Fe_2O_3. This fact of course makes a further analysis very difficult. Neither does it encourage a quantitative determination of the temperature coefficient of the effect.

Measurements at low temperatures (− 60° C) clearly revealed however that on cooling the relaxation times are increased, so that probably an activation energy is involved.

It seems probable that such large variations in τ as do
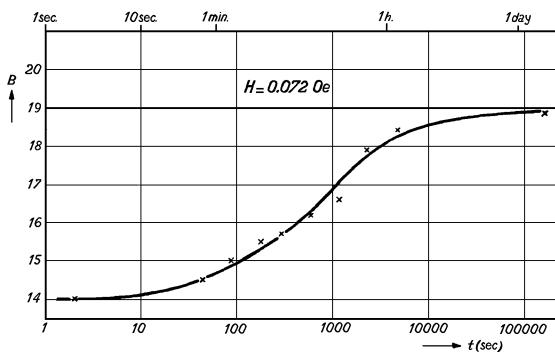
Fig. 22.
Magnetic after effect observed in the ferrite of Fig. 21.

actually occur in one specimen at a given temperature are due to the activation energy not being constant throughout the material. This energy itself seems to be of the same order of magnitude as the activation energy of the C and N ions in the lattice of α-iron (10.000° K).

There seems to be some reason to suspect an ionic after-effect here too. However, none of the metal ions seems to capable of diffusion at room temperature, so that more probably the effect is an electronic one. It might perhaps be compared to the phenomenon of fluorescence.

Our formal theory of D.A. immediately led us to expect a magnetic after-effect (and possibly also an elastic after-effect).

A magnetic effect was found indeed (Fig. 22) but a search for an elastic effect was fruitless. The adaptation of the Bloch zones to their surroundings therefore seems of a different type here than was encountered in the case of ions of C and N migrating in the iron lattice.

Summarizing we are inclined to suggest that the phenomenon really is an electronic one, a $3d$-electron apparently being brought into a state of increased energy by the magnetic treatment.

In this respect it would more or less resemble the high frequency after-effects to be discussed in the following sections, which in all probability are due to migrations of electrons.

The main difference would be that in the case of the manganese ferrites a d-electron apparently is caught in some "trap", from which it can be freed only by thermal agitation, whereas in the high frequency effects the activation energy is either absent or small.

§ 18. Magnetic after-effect at higher frequencies (h.f. m.a.) (electronic after-effect)

Phenomena of M.A. at frequencies of the order of 1 kC/sec and apparently not seriously affected by changes in the temperature have been repeatedly reported in the literature. Two methods of measuring in the main were followed: first of all the magnitude of the permeability was deduced from measurements of the electric skin effect on solid wires [1]. A shortcoming of this method is that an extrapolation of the results obtained for high frequencies via the region of lower frequencies down to the static value of μ_0 is usually omitted.

A comparison of the high frequency value of μ_0 to the "static" value obtained from ballistic measurements on one and the same specimen of pure and well-annealed iron was carried out by us. It revealed for pure iron in the annealed

[1] Cf. M. J. O. Strutt and K. S. Knol, *Physica*, **7** (1940) 635, where an extensive list of literature is also given.

state the existence of an important dispersion region below 100 kC, which had hitherto escaped notice [1].

A more direct and conservative method of measuring h.f. M.A. has been followed by H. JORDAN, [2] who made very careful *a.c.* measurements on laminated cores used in telephony and thus obtained evidence of the existence of small after-effects at frequencies as low as $\frac{1}{2}$ kC. This method closes the „gap" between measurements made at high and those made at low frequencies, but it unfortunately does not allow measuring at very high frequencies.

H.f. M.A. of course is most easily studied on non-metals. It was found by us to occur there in abundance and in various forms. Nevertheless by simply measuring μ_0 as a function of the frequency on thin laminae of high μ_0 iron, conclusive evidence of the strong h.f.M.A. in metals could also be obtained and will be described at the end of this section.

Experimental evidence obtained with both classes of materials point to one and the same conclusion: an increase in μ_0 generally is accompanied by an increase in the time of relaxation. Conversely when wishing to ban M.A. to the regions of very high frequencies, improvements can as a rule only be obtained at the cost of a marked reduction in the value for the permeability.

Considerations of this kind finally led us to a conception of a theory of h.f. M.A., in which the effect is explained formally as a frictional force acting on the Bloch zones. In this way the general effect of changes in μ_0 on the value of the critical frequency is easily explained, as we will show presently. Quite generally we have for the "static" value of the initial susceptibility χ_0

$$\chi_0 = \frac{\mathrm{d}I}{\mathrm{d}x} : \frac{\mathrm{d}H}{\mathrm{d}x}, \tag{56}$$

x denoting as before the displacement of a Bloch zone, I the saturation magnetization. The derivation of this relation is founded on the equation

[1] J. L. SNOEK, *Physica*, **7** (1940) 515.
[2] H. JORDAN. *El. Nachr. Techn.*, **1** (1924) 27.

$$H = \frac{\mathrm{d}H}{\mathrm{d}x} \cdot x \qquad (57)$$

connecting the "equilibrium" value of x with the value of the magnetic field H by means of the constant $\frac{\mathrm{d}H}{\mathrm{d}x}$. Now in order to generalize (56) by introducing a frictional force we only have to put

$$H = \frac{\mathrm{d}H}{\mathrm{d}x} \cdot x + \frac{\dot{x}}{A}, \qquad (58)$$

x denoting the variation of x with time (the reason why the constant before $\dot{x}$ is given the form A^{-1}, will become apparent in the next section). On putting $H = H_0 e^{j\omega t}$ and $\chi = \chi_0 \cdot e^{j\omega t}$ we readily find for χ as a function of ω

$$\chi(\omega) = \frac{\dfrac{\mathrm{d}I}{\mathrm{d}x}}{\dfrac{\mathrm{d}H}{\mathrm{d}x} + \dfrac{j\omega}{A}} = \chi_0 \cdot \frac{1}{1 + j\dfrac{\omega}{\omega_{cr}}} \qquad (59)$$

the critical frequency being given by

$$\omega_{cr} = A \cdot \frac{\mathrm{d}H}{\mathrm{d}x} \qquad (60)$$

Equation (60) is useful in explaining the effect of temperature on the after-effect of copper zinc ferrite (Cf. § 24).

If on the other hand we wish to investigate the effect of an annealing treatment on ω_{cr}, (60) should be put into the form

$$\omega_{cr} \cdot \chi_0 = A \cdot \frac{\mathrm{d}I}{\mathrm{d}x}. \qquad (61)$$

We may safely assume A and $\frac{\mathrm{d}I}{\mathrm{d}x}$ to be independent of the heat treatment. It is then shown by (61), that in measurements carried out at the same temperature on samples which have

been heat-treated in various ways ω_{cr}, may be expected to vary approximately inversely as the permeability.

An indication, that ω_{cr} decreases with increasing μ_0, is given by the following experiment: WOLMAN [1] as well as SCOTT [2], by comparing the measured changes in L and R of a coil containing a laminated core of a ferromagnetic alloy with the
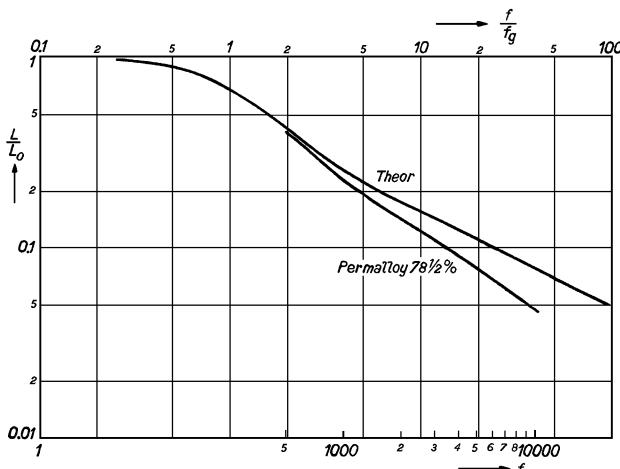
Fig. 23.

Curve showing the variation of $\dfrac{\mu}{\mu_0} = \dfrac{L}{L_0}$ with frequency for a laminated core of permalloy. $\mu_0 = 5100$; $\rho = 177 \times 10^{-6}$ ohm. cm; $d = 0.34$ mm; $f_g = 254$.

calculated changes, have found that apparently some other factor besides eddy currents is causing a time delay between B and H at frequencies above 1 kC. Fig. 23 shows SCOTT's results. The same kind of experiment was carried out by us in 1940 on an iron sample having an appreciably higher value of μ_0. The results of our measurements are plotted in the same way as done by SCOTT (Fig. 24). Obviously the after-effect has

[1] W. WOLMAN, *Z. techn. Phys.*, **10** (1929) 595.
[2] K. L. SCOTT, *Proc. Inst. Radio Engineers*, **18** (1930) 1750 *Bell Syst. Techn. Publ.*, B 620.
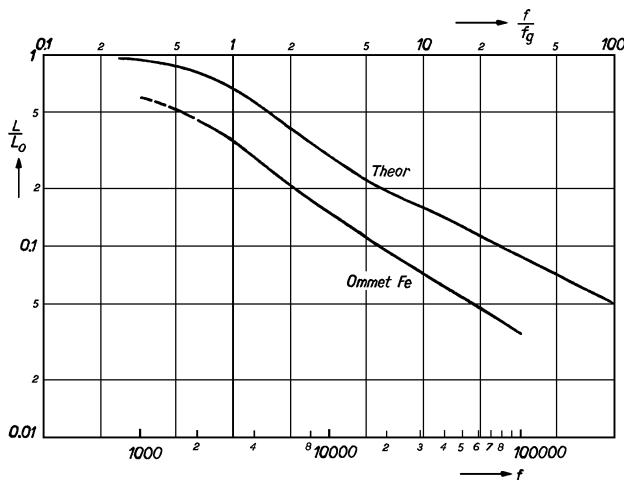
Fig. 24.

Curves showing $\dfrac{L}{L_0}$ for a sample of pure iron (measurements by KÖHLER and KOOPS). $\mu_0 = 1450$; $\rho = 9.8 \times 10^{-6}$ ohm. cm; $d = 152$ micron; $f_g = 3100$.

shifted to lower frequencies, thereby suggesting that indeed an increase in μ_0 causes ω_{cr} to decrease.

§ 19. The experiments of Sixtus and Tonks on large Barkhausen discontinuities

The hypothesis mentioned in the previous section requires a further foundation upon facts. As will be shown, evidence of the most convincing kind would be obtained, if one succeeded in obtaining large BARKHAUSEN discontinuities in a long cylinder of a ferromagnetic non-metal made anisotropic by elastic stress. Omitting in equation (58) the term which accounts for the internal stresses and the inclusions we obtain

$$\dot{x} = v = A \cdot H. \tag{62}$$

indicating that Bloch zones may be expected to travel in non-metals at a rate directly proportional to the field H and inversely proportional to the frictional constant A^{-1}.

Though evidence of this kind for non metals is still lacking,

it is highly satisfactory that the data obtained by K. L. Sixtus and L. Tonks [1] on elastically stretched wires of nickel iron strongly support our hypothesis. In these experiments v was found to be proportional to $H - H_0$ where H_0 is a constant measuring the effect of hysteresis and tends towards zero if the influence of the hysteresis is diminished. For hysteresis equal to zero we obviously may expect a relationship of the form (62) to hold.

In the summary of their first paper on this subject the authors declare categorically: "A is nearly constant for changes in tension, in diameter of wire, for composition of wire and is the same for a strip. Its value is approximately 25,000 cm sec^{-1} gauss^{-1}"

In the second paper [2] this important result is camouflaged more or less by attempts to bring it in harmony with certain formulae for the penetration time δt developed under the assumption that eddy currents are the sole cause of the retardation of the Bloch zones.

δt is calculated to

$$\delta t_1 = 3.94 \cdot 10^{-8} \cdot a^2 \cdot \frac{\Delta I}{\varrho \, \Delta H},\tag{63}$$

whereas the experiment gives

$$\delta t_2 = 3.94 \cdot 10^{-8} \cdot 0.035 \, a \cdot \frac{\Delta I}{\varrho \cdot \Delta H}.\tag{64}$$

In these formulae a is the radius of the (circular) wire, ΔI and ΔH represent the discontinuities observed in I and H at the Bloch zone. No explanation for the discrepancy between (63) and (64) is offered by Sixtus and Tonks.

Examining the experimental results in the light of our theory of magnetic after-effect, it is evident that they can be interpreted as follows: The observed time δt cannot possibly be smaller than the calculated time; so it is certain that the experimental formula (64) cannot hold for values of a much

[1] K. L. Sixtus and L. Tonks, *Phys. Rev.*. **37** (1931) 930.

[2] *Phys. Rev.*, **42** (1932) 419.

larger than 0.035 cm. Examination of the actual data shows that indeed no values of a have been examined, which greatly exceed 0.035 cm (cf. Table II).

TABLE II

Diameter of wire (cm)	ΔH (Oe)	v (cm/sec)	$A = \dfrac{v}{\Delta H}$
0.013	0.39	7.400	19.000
	0.63	11.600	18.400
	0.87	15.800	18.200
	0.97	17.800	18.400
	1.21	22.000	18.200
0.026	0.31	6.500	21.000
	0.66	15.000	22.700
0.038	0.11	2.100	19.100
	0.47	8.800	18.700
	0.69	13.800	20.000
	1.04	21.600	20.800
0.053	0.21	2.500	11.900
	0.44	6.000	13.600
	0.67	10.000	14.900

On the other hand experimental values for δt may be expected to turn out larger than the theoretical values, if another retarding factor besides the eddy currents is active. The fact that for small values of the radius δt becomes smaller and smaller with respect to δt_2 shows that for small cross-sections a new retarding effect prevails over the retardation caused by eddy currents.

An inspection of the data provided by the authors in their second paper shows that, for small values of a, A really takes on constant values.

For larger values of the diameter we find a slight decrease in A, which no doubt marks the gradual transition to conditions, where eddy currents are more important than after-effect. Of course the fact has to be considered, that the Bloch zones in the experiments of SIXTUS and TONKS are not flat, but have

the form of a cone. The absolute velocity of parts of the Bloch zone situated at some distance from the opening of this cone no doubt is very much smaller than the velocity of the cone as a whole. The displacement of the Bloch zone will probably most seriously be hampered by h.f. M.A. at the opening of the cone, a situation which is just the reverse of the one met with the eddy currents.

§ 20. THEORY OF H.F. M.A. (SPIN SPIN RELAXATION)

It remains to be discussed how the factor A in the relation

$$x = v = AH \tag{62}$$

might possibly be explained.

The theory advanced here is founded on certain considerations put forward by J. C. SLATER [1]. As shown by SLATER in 1930 and amplified by K. F. NIESSEN [2] in 1939, the interaction energy between two d-electrons mainly consists of a part corresponding to the situation, arising when two d-electrons are meeting at the same ion; the remaining terms contribute only $\frac{1}{2}\%$ to the total energy. In physical terms this obviously means that the interaction takes place only when two d-electrons meet at the same atom. During the time between two such "meetings" according to SLATER's picture transfer of magnetic energy from one spin to another should not be possible.

We wish to know the order of magnitude of this time τ^*. It is known from general considerations that the frequency v at which an electron in an energy band is moving from one atom to another is given by the relation

$$h \cdot v \backsim E \tag{65}$$

where E represents the width of the band (about 5 el. volts $= 5 \times 1.59 \times 10^{-12}$ erg in the case of the $3d$-band).

Assuming that nearly each "jump" of a 3 d-electron from one atom to another leads to a fresh meeting between two

[1] J. C. SLATER, *Phys. Rev.*, **49** (1936) 537, 931.
[2] K. F. NIESSEN, *Physica*, **6** (1939) 1011.

spins — an assumption which seems not altogether unreasonable — we find for the time τ^*

$$\tau^* = v^{-1} \sim 1 \times 10^{-15} \text{ sec.} \tag{66}$$

We now shall try to visualize the actual way in which a Bloch zone may move through a ferromagnetic body under the action of an external field H. We suppose hysteresis and eddy currents to be absent.
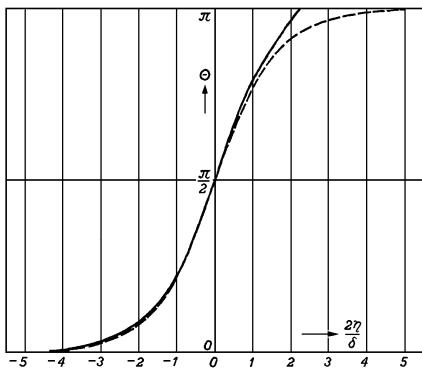
Fig. 25.

Variation of Θ with $\dfrac{\eta}{\delta}$ inside a Bloch zone (Θ is the angle between the spins and the field, δ the width of a zone, η the distance along an axis normal to the zone). Dotted line : curve for $H = 0$. Drawn out line : curve for $H = 0.1\, H_m$ (H_m = the molecular field $= k \cdot \Theta_B$).

As the initial state we may picture a state in which by some means or another, spins having negative x (x denoting a distance from a certain point along a direction lying parallel to the external field) are lying antiparallel to the field, while spins having positive x lie parallel to the field. (Cf. Fig. 25).

In the neighbourhood of $x = 0$ the transition from antiparallel to parallel orientations takes place in steps covering a certain number of spins assumed to be of the order of a hundred.

It is known that in such a model the application of a very small magnetic field suffices to make the Bloch zone move.

The energy required to accomplish this displacement can be made very small, indeed virtually zero. The flow of energy taking place from one spin to another during the displacement is however decidedly different from zero. A certain spin, while changing over from an antiparallel position to a position

normal to x, is receiving the required energy from its neighbour. Afterwards it gives off energy to help other spins to change position. Once having passed this perpendicular position, energy is gradually passed on by the spin — more being given off than is received — until the spin lies in a position parallel to the external field. (The field is always assumed to be infinitesimally small).

It will be clear, that this energy transfer taking place inside a moving Bloch zone is a process taking some time and that the relaxation time τ^* somehow will be involved in the process.

The calculation which we are now going to give is of a very provisional nature, but at least has the merit of making a first "breach" into this very difficult problem.

Following PIERRE WEISS we shall describe the interaction between spins as a "molecular field" acting on the spin and define the latter formally by

$$k\Theta = \mu_B \cdot H_m \tag{67}$$

where Θ is the Curie temperature, k the BOLTZMANN constant, μ_B the BOHR magneton. If the external field is zero, the mean equilibrium of a spin inside a Bloch zone is somewhere between the parallel and the antiparallel position. If an external field H_e is now applied, this mean equilibrium position is shifted by an angle Ψ given by

$$\Psi = \frac{H_e}{H_m} \tag{68}$$

We now assume that each time interaction is taking place between two neighbouring spins the change of azimuth "handed over" from one spin to another is of the order of the angle Ψ defined above.

The rest of the calculation is very simple. The total angle π over which the spin has to be turned is divided into n steps. n being given by

$$n = \frac{\pi}{\Psi} = \pi \cdot \frac{H_m}{H_e} \ . \tag{69}$$

In the time

$$t = n\tau^* \qquad (70)$$

required for the change over from an antiparallel to a parallel position, the zone has displaced itself over a distance of the order of its own width δ. The velocity $\dot{x} = v = \dfrac{\delta}{t}$ is thus

$$v = \delta : \pi \cdot \frac{H_m}{H_e} \cdot \tau^* = A \cdot H_e,$$

in which

$$A = \frac{\delta}{\pi H_m \tau^*} \cdot \qquad (71)$$

With $\Theta = 500°$ k, $\delta = 4.10^{-5}$ cm, A is found to be equal to 1000 cm/sec^{-1} gauss^{-1}, which is of the right order of magnitude, taking into account the very rough nature of our estimate.

It remains to be discussed whether the value of A thus found is really a constant in the sense indicated by the experiments of SIXTUS and TONKS.

According to our theory the external stress would indeed have some effect upon A, δ decreasing as the inverse square root of the stress. It is known however that the range over which the stress actually can be varied is not very large. The prospects for a verification of our statement are therefore not very hopeful. On the other hand there are no serious discrepancies with experimental findings obtained so far.

The denominator of (71) seems to contain only factors, which are variable within narrow limits; for instance H_m contains the Curie temperature Θ, τ the width of the $3\,d$-band. A further possible source of variations in A is formed by variations in the "mean free path" of the $3\,d$-electron. In our provisional calculation this path was supposed to be equal to one atom distance.

To all practical purposes A is to be considered as a constant and the experimental results so far are thus more or less accounted for. While attempting to find a further justification for equations (68) and (69), we have been led to calculate

the change in the shape of a Bloch boundary zone caused by the presence of an external field. In order to be able to do so, it is necessary to assume that in a certain region spins lying antiparallel to the field are unable to change their position.

The calculation is very simple. It is given in short form in Appendix V. Fig. 25 indicates the change brought about by an external field. The position of the front of the Bloch zone is characterized by a discontinuity in the first differential quotient. In a freely moving zone this discontinuity would probably be absent.

We end this section with a general remark. Theories of solids as a rule have had as their sole object the explanation of properties characteristic of the condition of static equilibrium, such as density, elasticity, etc.

Problems involving time are seldom attacked. As far as the author is aware only the electrical properties, and these until now only very summarily, have given information about such things as a mean free path and times of relaxation of the electron. Now an interesting possibility of obtaining information of this kind is opened up by a study of h.f. M.A. in ferromagnetics. Especially in non-metals, experimental conditions seem most favourable. The present outline is little more than a first introduction into this new field, which will undoubtedly take a number of years to explore.

New experiments seem to indicate that the theory given above requires considerable modification. Especially our explanation of the frictional constant A in terms of a spin spin interaction is now open to serious doubt.

III. DEVELOPMENT OF MAGNETIC MATERIALS

§ 21. NON-METALS VERSUS METALS IN FERROMAGNETISM

The use of ferromagnetic non-metals (mainly oxides) is very old, older perhaps than the use of metals. Permanent magnets made of magnetite (Fe_3O_4) are among the first ferromagnetic objects known. The largest saturation value observed for the non-metals being only about one third of the saturation value of iron, it goes without saying that for all purposes, where a high value of the induction is essential, alloys having iron as the main component are superior to the non-metals.

It has been realized at an early date, that ferromagnetic non-metals with their high specific electric resistance should be useful materials for h.f. purposes. With the gradual development of metallurgy however, attention soon was turned from the non-metals and almost exclusively given to metals and alloys, even in cases, where the high conductivity constituted a serious obstacle to their use.

The amount of work spent on the development of powder cores suitable for use at frequencies ranging from 1– 1000 kC is enormous. The permeabilities of these compound cores range from about 100 to values of less than 10 for the highest frequencies.

It had since long become obvious to those working in the field that at the highest frequencies eddy currents are not the only source of losses. High frequency after-effects are however difficult to study on metal cores and their theory did not develop.

As to hysteresis the whole attention spent on this problem was also turned in the direction of metals. High μ-alloys like permalloy and sendust have been the main result.

In this laboratory the systematic research on ferromagnetic non-metals both as to hysteresis and as to after-effect was taken up in 1933 [1] and has been carried on during the war with increasing intensity.

New materials with exceptionally low hysteresis as well as very low losses at high frequencies have been developed as a

[1] J. L. SNOEK, *Physica*, 's-Grav., **3** (1936) 463.

result of this work. For them the general trade name "ferroxcube" has been reserved.

The new "ferroxcube" materials are not of course malleable like many of the metal alloys. They prove however easily workable by grinding and lapping, and may be given very flat surfaces at little cost. Joints of "ferroxcube" surfaces tend therefore to show a much smaller magnetic resistance than joints in metals circuits. Laminating of course is no longer necessary.

Altogether four different types of ferroxcube have up till now been developed and their usefulness for the most varied purposes, all of which however involve high frequencies has been amply proved.

It will be our aim to describe and explain in the following sections some of the properties of the ferroxcubes prepared in this laboratory. Magnetic as well as more generally physico-chemical properties are to be recorded.

To a certain extent the ferroxcubes represent a "meeting place" for certain very general laws found to hold good for ferromagnetics and some equally general laws which are valid for all sintered bodies. As few readers are acquainted with both fields of activity alike, a little more explanation than usual may be necessary here and there.

In respect of the high frequency after-effect (h.f. M.A.) entirely new laws have been found, the essence of which has already been summarized in the introductory chapters. To explain these new results as well as the properties of ferroxcube with regard to hysteresis, the derivation of a few new formulae will also be required.

§ 22. The cubic ferrites

Substances having the general formula $MO . Fe_2O_3$ (in which M stands for a bivalent metal ion), are chemically known as ferrites. A number of these ferrites, notably the ones containing the bivalent ions of Mg, Zn, Cu, Ni, Fe, Co, Mn have a cubic structure and can be made to form mixed crystals at will.

As pointed out by FORESTIER [1] the bivalent ions mentioned above are all about equal in size. Introduction into the lattice of larger ions such as Pb or the ions of the earth alkalis leads to hexagonal structures. Polycrystalline aggregates of non-cubic crystals generally tend to form internal stresses on cooling on account of differences in the coefficient of expansion, and, moreover, are as a rule, strongly anisotropic. The absence both of a strong anisotropy and strong internal stresses is a *conditio sine qua non* for a low hysteresis. These non-cubic ferrites seem of little practical use. Only the cubic structures will therefore be dealt with.

Our choice of the bivalent ions is then restricted to the above-mentioned ions with only the possible exception of Cd and Ca, the ions of which are only slightly too large [2].

A systematic investigation of the magnetic properties of mixed crystals of the cubic ferrites revealed the interesting fact that those containing zinc ferrite have higher permeabilities than the rest. This seemed at first the more remarkable, because zinc ferrite of all the ferrites mentioned is the only one which is unmagnetic. An explanation was soon found: by adding zinc ferrite the Curie temperature of a magnetic ferrite is lowered and the maximum of the permeability always found to occur just below the Curie point, may be shifted to somewhere near room temperature, preferably to a temperature slightly above it (Fig. 26). The temperature region between 10 and 40° C being considered important for practical use, the optimum proportions leading to a maximum for μ_0 between these limits were established for mixed crystals of Cu, Mg, Mn and Ni ferrite with Zn ferrite. The results are indicated in Table III.

TABLE III

Optimum proportions for obtaining high μ_0	Maximum μ_0 obtained
Cu : Zn = 20 : 30	1500
Mg : Zn = 25 : 25	700
Mn : Zn = 25 : 25	2000
Ni : Zn = 15 : 35	4000

[1] H. FORESTIER, *Comptes Rendus Paris*, **192** (1931) 842.
[2] Measurements made in this laboratory.

The maximum values recorded as obtained with these mixtures relate to ferrites containing the bivalent and trivalent oxides in exactly the equimolecular proportion.

The results obtained are dependent on the way in which these ferrites are prepared.

The most obvious method of preparation, consisting of mixing the oxides in the required proportion and melting them together, fails, as the melt gives off oxygen and is moreover violently attacked by the material of the mould. More refined methods of sintering which are common in ceramic technique, but which have also proved their worth for the preparation of some alloys, therefore have to be applied. Among them is the use of an "active" form of iron oxide.

Even then sometimes considerable care is required as will be illustrated by the case of the *Cu Zn* ferrite in § 24.

The test samples on which most of the measurements were made were prepared by pressing powder in a mould, giving it the shape of a ring of external diameter 35 mm, internal diameter 25 mm and approximate height 5 mm. The pressure applied usually was about three tons/cm². Before discussing the results obtained on various ferrites, it will be necessary to consider in some detail the nature of the measurements carried out and the formulae used in deriving from them numerical results bearing on the material.

§ 23. CONSTANTS CHARACTERIZING THE CORE MATERIAL "FERROXCUBE"

For materials in which skin effect is absent, an interesting relationship can be derived between the values of tan δ and μ as measured on a ring and the corresponding values tan $\delta_1{}^*$ and $\mu_1{}^*$ measured on a circuit with air gap. We make the usual simplifying assumptions that no leakage occurs outside the air gap and that the air flux parallel to the core (which is assumed to have a constant cross-section) may be neglected. Under these circumstances the well-known relation

$$\frac{1}{\mu_1} = \frac{\alpha}{\mu} + \beta \tag{72}$$

holds between the "effective permeability" μ_1 and the permeability μ of the core material, α denoting the fraction of the total magnetic path occupied by the core material and β the fraction occupied by "air". We have of course

$$\alpha + \beta = 1 \tag{73}$$

and so we are able to write

$$\frac{1}{\mu'} - 1 = \alpha\left(\frac{1}{\mu} - 1\right) \tag{74}$$

Introducing the reciprocal permeability or reluctivity $r = \dfrac{1}{\mu}$ we have

$$r' - 1 = \alpha\,(r - 1) \tag{75}$$

and accordingly

$$\Delta r' \quad = \alpha\,\Delta r, \tag{76}$$

where Δr is an arbitrary increment in r.

For given values of the maximum induction and the frequency, the permeability and the loss angle will have certain values independent of the width of the air gap. This fact can be accounted for by writing r as a complex quantity

$$r = \varrho + i\sigma \tag{77}$$

For not too large values of δ, $\dfrac{\sigma}{\varrho}$ is equal to the tangent of the phase angle δ between B and H. By choosing for Δr the imaginary part of the reluctivity we obtain

$$\Delta \sigma' = \alpha\Delta \sigma \tag{78}$$

which on dividing by ϱ' and ϱ develops into

$$\tan \delta' = \frac{\varrho}{\varrho'} \cdot \alpha \cdot \tan \delta \tag{79}$$

and making use of (74) into

$$\frac{\tan \delta'}{\mu' - 1} = \frac{\tan \delta}{\mu - 1} \cdot \frac{\mu \cdot \varrho}{\mu' \cdot \varrho'} \tag{80}$$

Equation (80) can be considerably simplified. For not too

large values of tan δ, μ and μ' can be identified with their real parts and the factor $\dfrac{\mu \cdot \varrho}{\mu' \cdot \varrho'}$ then becomes equal to unity. A further simplification is obtained by assuming — as is nearly always the case — that both μ and μ' are much larger than unity. We then obtain

$$\frac{\tan \delta'}{\mu'} = \frac{\tan \delta}{\mu} \tag{81}$$

or

$$\frac{R'}{\mu' \cdot f \cdot L'} = \frac{R}{\mu \cdot f \cdot L} \tag{82}$$

Equation (81) shows that a constant of the form $\dfrac{\tan \delta}{\mu}$ or $\dfrac{R}{\mu \cdot f \cdot L}$ is most useful in comparing the values of $\tan \delta'$ obtainable on a planned magnetic circuit with given μ', if core materials are available having widely different values of tan δ and μ .

Assuming that between B and H the well-known Rayleigh relation

$$B = aH + bH^2 \tag{83}$$

holds good independent of the frequency, the right-hand term of (82) can be split into two parts

$$\frac{R}{\mu \cdot f \cdot L} = \frac{R_h}{\mu \cdot f \cdot L} + \frac{R_r'}{\mu \cdot f \cdot L} = c_h \cdot B_0 + c_r (f). \tag{84}$$

the hysteresis coefficient c_h being equal to

$$c_h = \frac{16}{3} \cdot \frac{b}{a^3} . \tag{85}$$

For powder cores and laminated metal cores c_r may be written as the sum of an eddy current term $c_e \cdot f$, containing the frequency f and another — usually very small — term, which is independent of f and which accounts for the so-called "residual losses" [1].

[1] V. E. Legg, *Bell System Technical Journal*, **15** (1936) 39.

For ferrites this subdivision is of little use. The eddy current coefficient depends on the dimensions of the solid specimen, but in actual experiments it usually is too small to deserve special attention. If necessity arises it can moreover be easily calculated from the measured value of the specific electric resistance of the core material [1].

The residual losses on the other hand are found to be anything but independent of the frequency, so that instead of having a single constant c_r, we have to use a curve or a set of values giving c_r as a function of the frequency. On account of the frequency region explored ($2 — 1000$ kC) being rather large, c_r preferably is plotted against log f instead of f. In case tan δ is large, the value of μ will also be found to depend upon the frequency. In order not to introduce too many data this variation with the frequency will usually be ignored, the values given by us applying to a fixed frequency of 2 kC.

This same frequency was used in the determination of c_h. The hysteresis loop constant is of the order of 10^{-4} and the residual loss constant of the order of 10^{-6}. It is therefore useful to introduce the new quantities

$$C_h = 10^6 . c_h \text{ and} \tag{86}$$

$$C_r = 10^4 . c_r \tag{87}$$

and to use the values of C_h and C_r for purposes of comparison [2].

From the fact that (82) and (84) are also valid if the coefficient c_r is zero, it follows that measurements of the hysteresis on circuits containing air gaps can in principle be used for obtaining information about the material itself. In fact we have:

$$\frac{R'_h}{\mu' . f . L} = \frac{R_h}{\mu . f . L} = c_h . B_c.$$

[1] Due precautions have to be taken, that these measurements are not falsified by the presence of surface layers having different properties. By using a sonde method this source of errors can easily be circumvented.

[2] Cf. V. E. LEGG, *Bell System Technical Journal*, **18** (1939) 438. It will be found that our C_h is identical to the hysteresis coefficient $a \times 10^6$, used by LEGG in Table IV.

This relation may be made use of, when hysteresis losses are measured on a powder core. Actually the results obtained on a powder core are very often considerably inferior to what might be expected, taking as a basis data obtained for the same material in the solid form.

The causes for this decrepancy are obvious: on the one hand it is very hard to make sure that the powdered material is in the same magnetic condition as the solid material, with which it is compared. A second and most probably more important reason why the properties as to hysteresis of a loading coil are nearly always below expectation, lies in the fact that the air gaps are not of uniform widths. Variations in the width of the air gap lead to local concentrations of the flux, which in turn may lead to increased hysteresis. It is impossible at present to separate these two effects.

With circuits containing the solid material ferroxcube, having one or two air gaps of exactly uniform width equation (66) may be expected to hold accurately. Its actual validity has been tested repeatedly by W. SIX of this laboratory for various practical cases. There is no difference at all between the materials used in an open and in a closed circuit. For these and other reasons magnetic circuits built with ferroxcube cores compete favourably with circuits built for analogous purposes with powder cores (Cf. § 26).

A further advantage lies in the fact that the properties of arbitrary magnetic circuits containing ferroxcube can be calculated with reasonable accuracy from data obtained on the ring.

It goes without saying that the values of R_h/L measured on a closed ring with a permeability of two thousand are much more easily accessible to measurement than those occurring in a circuit in which the permeability μ' has been reduced to a value of one hundred by means of an air gap.

If the non-linear distortion present in the air gap is of the right magnitude it is so small as to make a direct determination impossible. This is one of the reasons why in specifications set up by the responsible authorities, limitations are only

imposed on the value of R_h/L and not on the magnitude of the higher harmonics, which is the more important quantity.

The direct determination of the non-linear distortion on rings made of ferroxcube is within the range of possibilities and has actually been carried out by J. W. L. KöHLER and C. G. KOOPS of this laboratory on many samples. Let

$$v = \frac{V_3}{V_1} \qquad (88)$$

denote the ratio of the voltages caused respectively by the third and the first harmonic in the magnetic circuit.

Between v and R_h/L the well-known relation exists

$$v = 0.6 \frac{R_h}{\omega L} \qquad (89)$$

Let further $\varDelta L$ represent the difference in the value of L measured for a given value of v_1 and the extrapolated value for $v_1 = 0$. Between $\dfrac{\varDelta L}{L}$ and $\dfrac{R_h}{L}$ we have the additional relation

$$\frac{\varDelta L}{L} = \tfrac{3}{4}\,\pi \cdot \frac{R_h}{\omega L}, \qquad (90)$$

which of course is even more easily verified.

The constants C_v and C_L mentioned occasionally in the tables indicate the ratio of the measured values of v and $\dfrac{\varDelta L}{L}$ to the values calculated from $\dfrac{R_h}{L}$. Usually these constants are only little different from unity.

Accurate measurements of $\varDelta L$, R_h and the distortion were made by KöHLER and KOOPS using an a.c. bridge of the MAXWELL type. All measurements of c_h and c_r up to a frequency of 100 kC were carried out on this bridge.

For higher frequencies the resonance method was used. Measurements were carried out under the direction of M.GEVERS. Usually the agreement between the curves for c_r obtained on both sides of the limiting frequency 100 kC was very good.

Occasional disagreements were traced back in some cases to insufficient extrapolation of the results to the limiting case $B = 0$, in other cases to exceptionally high dielectric losses.

Results obtained at the highest frequencies tend to be falsified again by dielectric losses and in some cases by eddy current losses. Except where specifically mentioned no special precautions were taken to obtain the highest accuracy at these top frequencies.

For a first orientation the accuracy of the c_r-curves as measured is entirely sufficient. It will be seen that the effect variations in the chemical composition and the method of preparation are much greater.

After it had been observed that appreciable deviations from the Rayleigh relation frequently occur in ferrites, it was decided to measure R_h/L at a number of widely different values of the current. A range of 0.1—5 mA was covered and a plot of R_h against i made.

In cases where R_h is found not to be proportional to i, the definition (85) of c_h only holds good for a fixed value of B_o. We have chosen as such $B_o = 7.5$ Gauss. Calculation shows that if the R_h-i curve is not straight, the actual non-linear distortion differs from the distortion calculated for a certain point of the curve assuming that the connection of this point with the zero point is a straight line only by a factor $\sqrt{2}$ at most. Details of this calculation will be published at a later date.

§ 24. Ferroxcube 1 (*Cu Zn* ferrite)

Two varieties of ferroxcube 1 are available. One named (a) is aimed at a high value of μ_0 ($\mu_0 > 1000$) and is useful as a core material for h.f. transformers and chokes. The second variety (b) has a lower μ_0 (200—300) and correspondingly a better h.f. characteristic. This material is used for permeability tuning up to a frequency of 1000 kC.

Of both qualities the composition roughly is: 20 mols of

Cu O, 30 mols of *Zn O*, 50 mols of Fe_2O_3. Small deviations from this proportion are possible without entirely changing the properties of the product.

While (*a*) is short of oxygen by a few tenths of a percent (*b*) is practically stoechiometric.

A high purity of the oxides is of course desirable, especially if high values of μ_0 are aimed at. Contamination by non-magnetic material of the mill may be avoided by using iron mills.

Ferroxcube 1*a* can be made in a number of ways. Much depends upon the condition of the iron oxide added to the mixture. In Table IV we give results obtained on a mixture containing a sample of pure Fe_2O_3, which had been heated to 1100° C before being added to the mixture. If more "active" Fe_2O_3 is used, the sintering temperatures are correspondingly lower. The symbol s.g. in the table stands for sintering for two hours at 900° C in oxygen followed by grinding for two hours in an iron mill. After this treatment had been applied respectively 0, 1, 2 and 3 times to a mixture made by hand the resulting products were pressed into the form of small test rings under a pressure of roughly four tons per cm² and sintered in oxygen at 1100, 1150, 1200 and 1250° C respectively. The resulting values of μ_0 (measured at 2 kC) are mentioned in Table V. The numbers between brackets are measured densities. It will be seen that the density of the product with the highest value of μ_0 differs only little from the value 5.38 deduced from X-ray measurements of the lattice-constant of the cubic cell ($a = 8.365$ Å). Curves showing the variation of μ_0 with temperature are shown in Fig. 26.
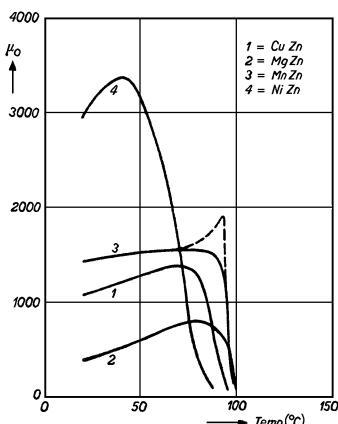

Fig. 26.
Curves for μ_0 vs T for various ferrites
1. *Cu Zn* ferrite 20/30 (Cf. Table **IV**)
2. *Mg Zn* ferrite 25/25
3. *Mn Zn* ferrite 25/25
4. *Ni Zn* ferrite 15/35

The products obtained by heating above 1150° C are very coarse grained and on breaking show at the fracture an intense black colour not unlike the colour of pitch. The specific electric resistance is about 20,000 ohm.cm, due to a measurable loss of oxygen (0.17 % by weight) taking place mainly during the last heat-treatment. It is not possible to make the lattice take up oxygen again by heating in oxygen at low temperatures, the mass being insufficiently porous for that.

TABLE IV

Cu Zn ferrite 20/30/50				
	1100° C	1150° C	1200° C	1250° C
Oxides mixed by hand	118 (3.60)	175 (3.75)	285 (4.05)	295 (4.45)
+ s.g.	148 (3.75)	260 (4.10)	390 (4.55)	1230 (4.85)
+ s.g.	154 (3.90)	310 (4.25)	450 (4.80)	1290 (5.00)
+ s.g.	155 (3.95)	340 (4.45)	1000 (4.95)	1580 (5.10)

The method indicated in Table IV of course is not the only one leading to a high value of μ_0. Values of μ_0 above 1000 may also be obtained by grinding only once. As an example we give the data mentioned in Table V. This table applies to two samples prepared from the same mixture, which had been ground for a period of roughly 200 hours, leading to a particle size smaller than one micron.

Values of μ_0 are given for three frequencies (2 kC, 100 kC and 1000 kC). The numbers between brackets again refer to measured densities. The symbols r.c. and s.c. refer to rapid cooling (in air) and slow cooling (in the oven) respectively. It is evident that a further continuation of the heat-treatment at 1000° C does not lead to greatly increased values of μ_0 or the density. A subsequent heating for one hour at 1200° C followed by rapid cooling leads to values for μ_0 in the neighbourhood of 600. Slow cooling on the other hand leads at once to $\mu_0 > 1000$. An additional heating at 1000° or 950° C does not produce any big change; rapid cooling (in air) from 950° C proves without effect on the value of μ_0.

TABLE V

Cu Zn ferrite 20/30/50 Oxide mixture ground once in an iron mill for 200 hours			
Heat-treatment	2 kC	100 kC	1000 kC
6 h. 1000° C s.c. (3.75)	112	112	112
+ 1 h. 1200° C r.c. (5.15)	590	590	580
+ 1 h. 1000° C s.c. (5.15)	1145	1052	758
+ 1 h. 950° C s.c. (5.15)	1120	1055	680
Heat-treatment	2 kC	100 kC	1000 kC
36 h. 1000° C s.c. (3.90)	130	130	130
+ 1 h. 1200° C s.c. (5.10)	1070	990	900
+ 1 h. 1000° C s.c. (5.10)	1040	1015	740
+ 1 h. 950° C r.c. (5.10)	1125	1030	645

From the fact that μ_0 is found to decrease strongly with frequency from 100 kC onward, it can at once be deduced that the loss angle becomes very large for these frequencies. As an illustration we give in Table VI values of tan δ for the samples mentioned in Table IV measured after the last but one heat-treatment.

TABLE VI

Loss angles of coarse grained ferroxcube 1					
v (kC)	tan δ_1	tan δ_2	v (kC)	tan δ_1	tan δ_2
2	0.027	0.030	200	0.173	0.197
16	0.056	0.063	500	0.325	0.386
40	0.080	0.094	750	0.418	0.413
100	0.141	0.158	1000	0.465	0.413

This large loss angle cannot in any way be ascribed to eddy currents, but is due to after-effect.

The mode of preparation of the b-quality of ferroxcube 1 differs from that of the a-quality in that care is taken to preserve a porous structure. After sintering, this porous sample

is allowed to take up oxygen at lower temperatures until a near approach to the stoichiometric ratio is made. By this treatment the relaxation time of the h.f. M.A. is reduced and a much better h.f. characteristic is obtained. The specific electric resistance is also increased by the treatment.

The porosity of the mass reveals itself in a number of ways.

In the first place the porous structure takes up water much more readily than a non-porous structure, a fact most vividly experienced, when such a sample is touched with the tongue. Secondly the fracture of a porous sample reveals a dull black colour approaching grey, which is considerably different from the shining black observed on the fracture of a non-porous structure. Thirdly X-ray analysis and inspection by the naked eye may be called to aid: "porosity" ceases to exist, as soon as the non-porous material has become coarse grained. A most important criterion of "porosity" of course lies in the presence or the absence of the ability of the material to take up oxygen when heated at temperatures below the sintering temperature. The determination of the change of weight of the specimens after heat-treatment sometimes offers a most useful means of asserting this.

The simplest method of preparing ferroxcube 1 consists of grinding the mixture only once for a fairly long time and sintering the pressed powder at once at the final temperature.

A second way consists of alternatively grinding and sintering the powder at comparatively low temperatures and grinding it again before the final sintering is done. This is a well-known means of ensuring a homogeneous final product in all chemical operations, where a reaction between two or more solid components is involved.

The beneficial effect of such a treatment on the permeability has already been shown for the a-quality. For the b-quality the criterion of the "porosity" is added and it cannot therefore be decided beforehand, which of the two processes eventually leads to the best product.

It has been found, that for ferroxcube 1 b the process of repeated grinding and sintering also presents some advantage

over the process in which a thorough grinding is followed
by pressing and the final sintering.

There are some interesting differences between the two
processes, which it may be worthwhile recording here. In
Fig. 27 the "simple" process (marked $1 \times s$) is compared
with a process in which intermediate sintering at 900° C was
carried out twice (marked $3 \times s$ in the figure). The upper
part gives the measured mean density as a function of the
final sintering temperature. The fact that the curve marked
$3 \times s$ lies far above the curve marked $1 \times s$ is in accordance
with our experience on type a of ferroxcube 1. So is the
middle part, where μ_0 is
plotted against the final
sintering temperature. The
lowest part of Fig. 27
however is the most in-
teresting one. It gives
C_r (f) for a frequency of
1000 kC/sec. The tempe-
rature at which C_r passes
through a minimum ob-
viously is the one to be
chosen in order to ensure
the best possible charac-
teristic at this frequency.
For $3 \times s$ this tempera-
ture is appreciably lower
than for $1 \times s$ and also
the minimum itself is
somewhat lower. It is a
curious fact, that *both* μ_0
and the density d for the
optimum temperatures of
sintering are found to
have about the same value
$\mu_0 \sim 400$; $d \sim 4.4$.

The two processes,
though different, seem
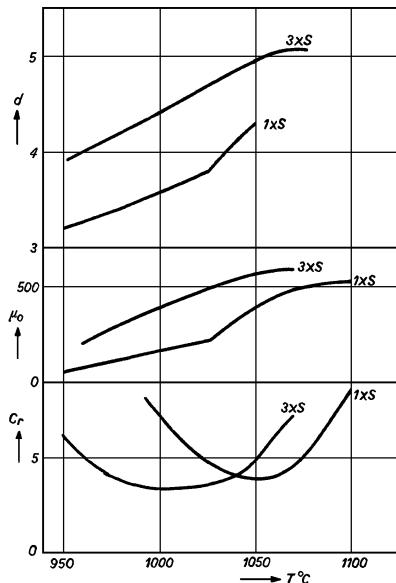
Fig. 27.
Plot of density, permeability and loss
factor at 1000 kC/sec. for *Cu Zn* ferrite
20/30 against the final sintering tem-
perature. Curves marked $1 \times s$ apply to
specimens sintered only once. Curves
$3 \times s$ apply to specimens which have
been sintered twice at 900° C before
final sintering.

therefore to lead to about the same results, when carried out under optimum conditions.

The above mentioned data are not to be taken as representing universal laws, from which no escape or deviation at all is possible, nor is the magnitude of the loss at 1000


Fig. 28.

Plot of loss factor against frequency for porous *Cu Zn* ferrite.

Curve 1 applies to nearly stoichiometric ferrite; the oxygen defect increases with increasing number of the curves and is only about 0.03% by weight for curve Nr 3.

kC/sec wholly decisive for the h.f. characteristic. Variations in the purity as well as the reactivity of reacting oxides or the addition of small quantities of other oxides may change the final result to some extent. The data given however do represent the general trend of things in the case of the *Cu Zn* ferrites.

We have not yet discussed the way in which the porous structure is made to take up oxygen. It is very simple. Heating in oxygen at temperatures ranging from 600° C downward to 400° C for a sufficiently long time suffices for the purpose. Some advantage may be found in previously heating for a short time at somewhat higher temperatures $(900 \to 700°$ C$)$ because at these temperatures diffusion and consequently the establishment of equilibrium is much more rapid and the total time required to ensure a good quality is thus shortened.

It is interesting to study the effect of the addition of oxygen on the curve for C_r. It proves to be fairly complicated. In Fig. 28 curve 1 represents C_r in a frequency interval from $2-1400$ kC for a ferrite sintered at 1050° C and then "saturated" with oxygen at low temperatures for a very long time. The value of μ_0 is found to be only 240; the curve for C_r (f) shows a flat and inconspicuous maximum at about 10 kC/sec, but remains

low right up to 1000 kC/sec. Another maximum in the losses evidently lies far beyond 1000 kC/sec.

A fresh heat-treatment at $1000°$C in oxygen followed by cooling in the oven causes the value of μ_0 to rise slightly, an effect which for the following may be entirely neglected. Due to the comparatively rapid cooling the oxygen uptake at low temperatures is now a little less complete. There now is a slight shortage in oxygen (probably of the order of 0.01% by weight), a fact which among others may be controlled by careful determination of the change of weight on samples having suitable dimensions. As a result of this very slight loss of oxygen, the low frequency maximum has shifted somewhat to the right and the h.f. maximum somewhat to the left, (Cf. Curve 2). The losses as a whole are somewhat higher, except for the lowest frequencies investigated.

A more important loss of oxygen (of the order of 0.03% by weight) is caused by quenching the sample in air from $950°$C, a treatment leading to values of C_r represented by Curve 3 in Fig. 28. Finally if the sample is heated in nitrogen at $950°$C in order to provoke the loss of some more oxygen, the two maxima unite and Curve 4 of Fig. 28 is the result. Curve 4 in its shape strongly resembles the curve found on ferroxcube a (dotted line of Fig. 28). In fact the only difference between the two probably is the greater porosity and perhaps a larger internal stress in the first-named sample. Curves of the type 4 correspond to an oxygen defect of about 0.2% by weight.

It is not possible at this stage of the investigation to say much about the physical background of the after-effect curves. A few words may suffice.

Our experiments have been carried on sufficiently far to show, that the l.f. maximum on decreasing the temperature shifts to lower frequencies. It is thus fairly certain that an activation energy is involved in the diffusion process underlying the after-effect responsible for this maximum.

The h.f. maximum is common to all ferrites investigated so far. The theory outlined in Chapter §§ 18—20 is thought to be applicable to this maximum.

The shift of the h.f. maximum with the temperature cannot

be determined as easily as for the l.f. maximum because of the high frequencies involved. Fig. 29 represents the result of a series of very careful measurements by LINDEN-HOVIUS of this laboratory on a sample prepared by precipitation of the hydroxides of *Cu, Zn* and *Fe* from a mixture of the nitrates by means of *Na OH*. These measurements were carried out at room temperature, and the temperatures


Fig. 29.
Curves for μ_0 for *Cu Zn* ferrite at three temperatures and at various frequencies.

of solid carbon dioxide and liquid air respectively. From this figure it seems to follow that the relaxation time depends upon the temperature in a most remarkable way: it seems as if τ becomes smaller as the temperature decreases. When we remember the general relation for diffusion

$$\overline{\Delta x^2} = 2\,Dt$$

this is a very astonishing result, as D is never found to rise with decreasing temperature. It follows immediately that something must be wrong with our tacit assumption that $\overline{\Delta x^2}$ does not depend on the temperature. The above evidence, combined with the fact that the value of μ_0 is profoundly affected by a change in the temperature, has led us to assume that the value of $\overline{\Delta x^2}$ may also be affected by changes in the temperature.

Following this line of thought we finally hit upon the idea already exposed in Chapter II § 18, that the lateral motion of a Bloch zone might be hindered by a frictional force of some kind. The observed increase of τ with increasing temperature can be explained on this basis, bearing in mind,
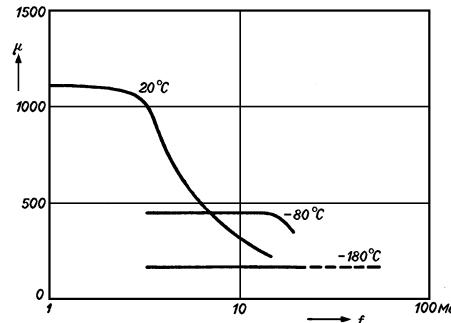
that λ is a quadratic function of I_{max}. As it is uncertain, which part the unmagnetic inclusions play in determining the initial permeability as compared to the effect of internal stresses, no quantitative theory could yet be developed.

We may end by adding a simple graphic illustration of h.f. M.A., which we have found most useful in explaining to ourselves the effect of an increase in μ_0 on the relaxation time τ.

Let in Fig. 30 the drawn-out curve represent the variation of the potential of a Bloch zone with the displacement x. The field H required to produce a certain displacement x_0 evidently is measured by the height of the point on the curve at $x = x_0$ above the minimum. In the case of the drawn-out curve this field is quite strong and μ_0 correspondingly low. A frictional force accompanying the lateral movement of the Bloch zone probably will be quite small compared with the field and so have little or no effect on μ_0. Suppose now, that by some means or other the potential minimum is "flattened" in the way indicated by the dotted curve. The "force" required to displace the zone over a distance x_0 is now much smaller and the permeability μ_0 correspondingly higher. Compared to this small force however, which even may be made equal to zero, the frictional force now has a much stronger effect and an after-effect may now be observed.

Fig. 30.

Drawn-out curve: shape of the potential minimum for a Bloch zone in a material with low μ_0. Dotted curve: same for a material with high μ_0. The force required to produce a certain displacement is much smaller now and a (constant) frictional force is now likely to produce a phase shift between B and H.

§ 25. FERROXCUBE 2 (*Mg Zn* FERRITE)

A suitable Curie temperature is obtained, if *Mg*-ferrite and *Zn*-ferrite are mixed in equal molar ratios. Figs. 31 and 32 show curves bearing on two series of samples. Both were prepared from 25 mols *MgO*, 25 mols *ZnO*, and 50 mols of Fe_2O_3 of the same kind as used for *Cu Zn* ferrite. The material of the first series of samples was only very superficially mixed and ground, the material of the second mixture
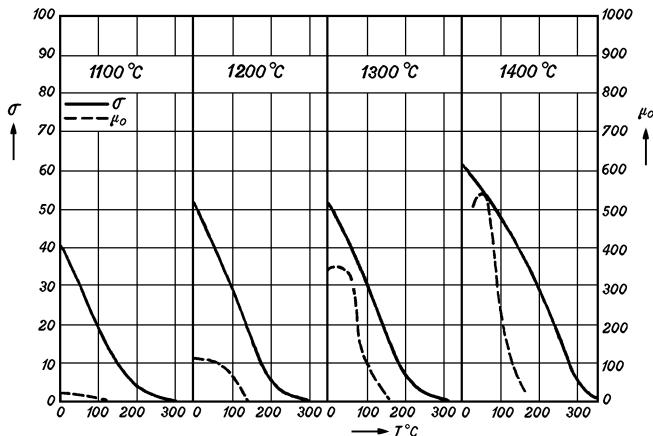
Fig. 31.
Mg Zn ferrite 25/25 coarse mixture.

was, on the contrary, ground to an extremely fine grain. Ring samples were prepared in the usual way and sintered in oxygen at 1100, 1200, 1300 and 1400°C respectively.

The drawn-out curves give measured values for σ, the saturation value of the magnetization per gram, as a function of the temperature. After sintering at 1100°C the coarse mixture has obviously reacted only very incompletely. The curves obtained after sintering at 1200 and 1300°C have about the same shape. The reaction now is practically complete. After sintering at 1400°C a new rise in σ as well as in the Curie temperature is observed. This rise is due to reduction of part of the iron oxide.

The dotted curves give μ_0 as a function of temperature. The thorough grinding has the effect of making the reaction at $1100°$ C much more complete.
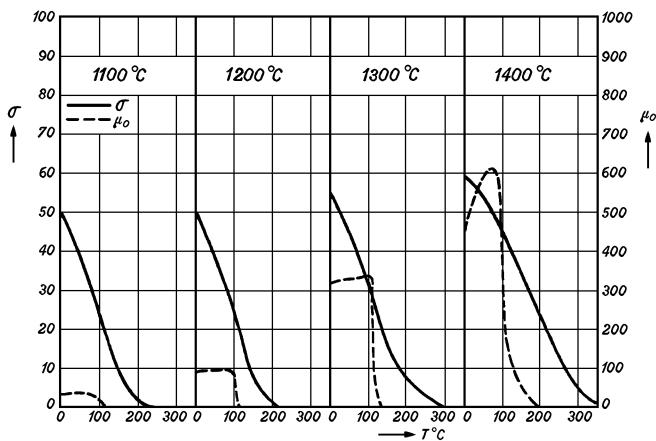
Fig. 32.
Mg Zn ferrite 25/25 fine mixture.

It is remarkable that the values obtained on the coarse mixture are not much inferior to those obtained on the fine grain. The top value of about 300 obtained after sintering at $1300°$ C is much lower than the top value obtained for ferroxcube 1. This is due among others to the magnetostriction being large: sintering at $1400°$ C which leads to the production of ferrous ions also leads to an appreciable increase in μ_0 (till about 600). It is not certain, whether the failure to reach a value above 1000 is due to insufficient suppression of the magnetostriction alone or besides that to an abnormal behaviour of the crystal anisotropy. Values of tan δ obtained at high frequencies (cf. Table VII) show that the coarse mixture is considerably inferior to the fine-grained mixture.

As can be judged from the fall in the specific electric resistance the fine-grained sample after sintering at $1300°$ C suffers a certain amount of permanent dissociation (0.17% by weight as determined by chemical analysis). It is more than probable that at $1300°$ C both the fine-grained and the coarse-grained

TABLE VII

Mg Zn ferrite 25/25/50

Coarse mixture

After sintering at:

1200° C $\mu_0 = 102$			1300° C $\mu_0 = 247$		
f (kC)	tan δ (%)	C_r	f (kC)	tan δ (%)	C_r
340	2.2	14	268	4.4	11
500	3.0	18	500	7.3	18
750	3.9	23	750	12.2	31
1000	5.0	31	1000	17.4	44
1400	8.0	48	1300	23.0	58

$\rho = 3.9 \times 10^5$ ohm.cm, $d = 3.3$ | $\rho = 1.8.10^5$ ohm.cm, $d = 3.55$

Fine-grained mixture

After sintering at:

1200° C $\mu_0 = 92$			1300° C $\mu_0 = 315$		
f (kC)	tan δ (%)	C_r	f (kC)	tan δ (%)	C_r
388	1.5	10	285	2.1	4.2
500	1.6	11	500	3.0	6.2
750	1.8	12	750	4.2	8.2
1000	2.0	14	1000	5.6	11.2
1400	2.4	16	1400	10.0	19.8

$\rho = 7.8 \times 10^5$ ohm.cm , $d = 3.6$ | $\rho = 6300$ ohm.cm , $d = 4.32$

mixtures are partly reduced, only the fine-grained sample owing to its greater density has lost more of its ability to take up oxygen again at lower temperatures.

This permanent loss of oxygen is an undesirable feature, both as to after-effect and as to eddy currents. As on the other hand a complete reaction and a high density proves benificial to the permeability, a compromise has to be sought. Table VIII gives an example of one of the many ways in which optimum conditions may be realized. The experiments, the results of which are recorded in this table, again relate to a mixture

containing 25 mols MgO, 25 mols ZnO and 50 mols Fe_2O_3; the last named oxide was this time prepared from the oxalate by heating at $650°$ C in a controlled atmosphere.

TABLE VIII

Mg Zn ferrite 25/25/50

Last operation sintering at:

	1200° C			1300° C		
	μ_0	C_r ($f=1000$ kC)	d	μ_0	C_r ($f=1000$ kC)	d
Mixed $\frac{1}{2}$ hour	250	13	3.65	400	high	4.4
+ s.g. (800° C)	295	10	3.8	395	high	4.55
+ s.g. (900° C)	275	7.5	3.8	405	16	4.6
+ s.g. (1000° C)	315	6.4	4.1	420	high	4.7
+ s.g. (1100° C)	225	8.3	3.7	370	8.0	4.6

Optimum values for μ_0 and the density are reached, if the last intermediate sintering treatment is carried out $200°$ C below the final temperature. Obviously a material which has been sintered too high in an intermediate treatment loses much of its ability to react a second time, the subsequent grinding process being insufficient for a full restoration of the activity.

While however after sintering at $1200°$ C the losses are a minimum under these conditions, they become unmeasurably high, if sintering is done at $1300°$ C. Dissociation now occurs in a structure, which at the same time becomes non-porous.

The above-mentioned features (with variations as to detail) are common to nearly all other ferroxcubes, whether the element magnesium has been replaced by another element, or the proportion of Fe_2O_3 to bivalent oxide is changed a little, or that small additions of another oxide are made.

The best way of obtaining a really good h.f. characteristic, evidently consists of ensuring a complete reaction between the solid components at the lowest possible temperature. Means of attaining this are discussed in the section on ferroxcube 4 (nickel zinc ferrite), where conditions are especially favourable.

The only feature of ferroxcube 2 which compares favourably
to all other ferroxcubes is its exceptionally low density. For
purposes, where a low weight is essential, this material might
therefore be useful.

§ 26. FERROXCUBE 3 (*Mn Zn* ferrite)

Ferrites containing manganese differ from other ferrites in
that oxidation may easily be carried too far, the element
manganese having the tendency to change into a higher state
of valency than two.

Also there is some uncertainty as to whether some of
the manganese ions under certain circumstances are able
to take the place of the trivalent iron ions in the spinel
lattice.

If a mixture containing 25 mols MnO (or a higher oxide),
25 mols ZnO and 50 mols Fe_2O_3 is prepared in the usual way,
the properties of the sintered product are found to be strongly
variable. Sometimes high values of μ_0 and σ are obtained,
another time the product is nearly unmagnetic. The explanation
is simple: all depends on the amount of oxygen the sample
picks up from the surrounding gas during cooling. This in
turn is found to depend upon the porosity of the structure
and upon the presence or absence of certain minor consti-
tuents acting as catalysts.

Porous structures of *MnZn* ferrite of course are difficult
to handle and cannot be trusted to lead to constant results.
As a matter of fact some porous samples prepared by us had
to be severely quenched in order to become magnetic; other
samples took up oxygen much less rapidly.

In the case of the manganese zinc ferrites, conditions are
such that a non-porous structure is desirable, if constant
results are to be obtained. In the presence of silicon dioxide or
another substance acting as a flux, a dense structure is easily
obtained at relatively low temperatures (1250 or 1200° C). The
permeability of such samples however does not acquire the
highest values, due to the material being heterogeneous.

With purer samples sintering has to be done at a higher

temperature and conditions are somewhat more critical; very high values of μ_0 are however obtained.

Once a non-porous structure of the required composition is obtained by sintering, it proves very stable under oxidizing conditions. Many hours of heating in oxygen at temperatures between 800 and 1000°C are needed to induce the manganese, once it has been nicely "built in", to adopt a higher state of oxidation. The process itself can be easily followed by the resulting decrease in μ_0 and σ (σ is the magnetization per gram). Conversely it will be clear that the amount of oxygen has to be controlled carefully during sintering and cannot be corrected afterwards.

Very good and well defined results are obtained on oxide mixtures of commercial quality, if sintering and cooling are carried out in nitrogen containing only traces of oxygen. Samples thus prepared also suffer very little from the phenomenon of D.A. described in § 17; they are homogeneous and magnetically very weak.

Samples containing some Fe_2O_3 in excess were also studied. It goes without saying that under the given circumstances this excess amount enters into solid solution with the ferrite in the form of Fe_3O_4.

If care is taken that the amount of excess of Fe_2O_3 and the total amount of oxygen are adjusted so as to produce a homogeneous product with magnetostriction equal to zero, exceptically low values are obtained for the hysteresis loopconstant C_h.

Samples having a low value of C_h were systematically sought for and occasionally found in the ternary systems:

Cu-ferrite — Zn-ferrite — Fe_3O_4 and the corresponding ones with Mg and Ni. Nowhere however were low values of C_h obtained as easily as in the ferrites with manganese.

The causes of this exceptional behaviour may be manifold and will not be discussed here.

The anisotropy of the magnetostriction and the crystal anisotropy may be very weak. It is hard however to find a suitable basis for comparison as long as nothing is known with certainty about the possible valencies of Mn in the spinel lattice.

There are indications that reactions between the partners in the mixture of MnO_2, ZnO and Fe_2O_3 are more complete than in other ferrites. To a certain extent this follows — besides from the high value of μ_0 — from the shape of the curve for the residual losses. The h.f. maximum lies somewhat above or below 1000 kC according to the oxygen content, and the loss angle is large in that region. On the low frequency side of this maximum however the loss angle goes down to values, which are smaller than are observed on any other ferrite. This may be partly due to the complete absence of the l.f. maximum. We have learned however from experience on ferroxcubes 1 and 2, that an incomplete reaction also leads to increased losses at low frequencies; this probably is due to a scattering in the value of the h.f. relaxation time. (Our theory of § 18 predicts such a scattering in τ for materials having irregular internal stresses). The very low losses observed may be taken as a sign that the reaction has been complete.

One final remark may be made about the l.f. maximum. We have found it most clearly in the copper zinc ferrites. We have seen that a small change in temperature produces a large shift in the frequency corresponding to this maximum. It might therefore easily have escaped detection in other ferrites. As a matter of fact some *Mg Zn* ferrites showed a small increase in tan δ near 2 kC, which might be taken as an indication for the existence of a l.f. maximum. Furthermore manganese zinc ferrites cooled in oxygen and displaying D.A. and M.A. (cf. § 17) may formally be said to have a l.f. maximum at frequencies of the order 0.01 cycle/sec.

At present it does not seem possible to make any definite statement regarding the l.f. maximum. We have only put the general situation before the reader and the drawing of more definite conclusions must await further developments.

We will now give some numerical results obtained with manganese zinc ferrite.

Table IX gives the values of μ_0, C_h, ϱ (in ohm.cm) and C_r for two typical cases, one having high μ_0 and low C_h, the other having a somewhat lower μ_0 and higher C_h, but a better h.f. characteristic.

TABLE IX

Properties of ferroxcube 3

	f (kC)	C_r (f)		f (kC)	C_r (f)
$\mu_0 \sim 1500$	2	0.1	$\mu_0 \sim 600$	2	0.3
$C_h \sim 1.6$	10	0.1	$C_h \sim 3,0$	10	0.4
$\rho \sim 50$	20	0.2	$\rho \sim 50$	20	0.6
$C_v \sim 1$	100	1.0	$C_v = 0.8\text{-}1.2$	100	1.2
$C_L \sim 1$	200	2.0	$C_L = 0.8\text{-}1.2$	200	2.4
	400	10.0		1000	6.3

Values obtained for C_r at the highest frequencies probably are a little too high, as no correction for eddy current losses has been made. The specific electric resistance of 50 ohm. cm is the lowest recorded so far for the ferroxcubes, and strongly reduces the interval between the frequency where losses due to after-effect become high, and the frequency where eddy current losses are getting high for a thickness of 5 mm. For frequencies below 100 kC neither of these effects makes itself felt however and the losses recorded are the lowest observed so far in any ferrite. Making use of such a ferrite it has proved possible to make a set of filters in which each coil occupies a volume of only 42 cm³ and has a Q of 600 at 60kC/sec.

C_h is practically independent of the maximum induction. The constants C_v and C_L accordingly are only slightly different from the theoretical value of unity (cf. § 24).

We will end this section with a short discussion of the various ways in which low values of C_h have been realized. The left half of Table X contains values of C_h measured on practical loading coil core materials, while the right half shows values measured on solid samples of the same or approximately the same composition. The values mentioned in the table are mainly derived from a compilation of relevant data by V. E. LEGG in 1939 [1].

The first two members of the series are anisotropic and

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[1] Cf. V. E. LEGG, *Bell Syst. Techn. J.*, **18** (1939) 438. It will be found that our C_k is identical to the hysteresis coefficient $10^6.a$, used by LEGG in Table IV.

TABLE X

	μ'	C_h	C_{hm}	μ	
Fernicube [1]	82	2.0	2.0	82	Fernicube
Isoperm	85	2.3	2.3	85	Isoperm
Permalloy	75	5	0.2	9000	Permalloy
Mo-Permalloy	125	1.6	0.05	22000	*Mo*-Permalloy
Sendust	47	4.5			
„	65	5.0	0.03	55000	10-6 Sendust [1]
„	102	8.5			
Iron Grade B	35	50			
Iron Grade C	26	80			
Carbonyl Iron 1 [1]	13	5	50	250	Magnetic Iron
„ 2	18	12.8			(900° C Pot)
„ 3	50	9.3			
Ferroxcube 3 [2]	—	1.6	1.6	2000	Ferroxcube 3

have no air gap. The values of C_h obtained depend exclusively on the degree of perfection with which spins are aligned in certain "preferred directions" and are the same for the solid material as for the core as a whole.

The last member is ferroxcube 3. As explained before the value of C_h measured on a core with an air gap is found to be independent of μ' and exactly equal to the value measured on the closed ring.

The remaining members of the series all represent powder cores and their properties are compared to those of solid specimens of the same type.

It has already been mentioned, that the Permalloys and the material Sendust like ferroxcube 3 have low hysteresis due to the fact that the conditions $E_c = 0$ and $\lambda = 0$ have been realized here in various degrees of perfection. It is at once noted, that the values obtained on the powder cores are inferior to those obtained on solid samples of approximately the same composition. As explained before this probably is due to imperfections in the system of "air gaps".

[1] M. KERSTEN, *Elektrotechn. Z.*, 58 (1937) 1335, 1364.
[2] Measurements made in this laboratory.

Powder cores made of ordinary iron as expected are bad, due no doubt to hysteresis of the inclusion type, the crystal anisotropy being very large. There is one apparent exception: Carbonyl iron 1 with $C_h = 5$ is decidedly better than is expected for a substance with $E_c \neq 0$ under ordinary conditions. This however probably is an example, where $\dfrac{d}{s}$ has been made high as a result of the introduction of large amounts of unmagnetic material into the substance: it is known that the iron used in these cores is made to take up nitrogen in large quantities during segregation from the gas phase. This leads to the formation in the iron of relatively large quantities of the nitride Fe_4N.

On the whole therefore the agreement between theory and observed data is satisfactory and the trend of future development clear. Non-metals having in the solid state values of C_h approaching those found for permalloy and sendust, evidently must surpass other materials when used with one or two air gaps in series instead of the very imperfect system of numerous small air gaps applied in powder cores on account of the necessity to suppress eddy currents.

§ 27. Ferroxcube 4 (*Ni Zn* ferrite)

We have repeatedly pointed out above that an ideal ferrite for h.f. use should:
1. not have a too high μ_0
2. nevertheless have a high saturation magnetization
3. contain no ferrous iron
4. nevertheless have a dense structure.

In order to be able to combine conditions 3. and 4., it is advisable that the ferrite should be formed as completely as possible at low temperatures. This may be done by precipitation from a solution containing the metal ions in the prescribed proportion. It is also desirable that the ferrite formed should should not easily lose oxygen at high temperatures, nor at low temperatures take up so much oxygen (manganese) that the ferrite becomes unstable.

All these conditions seem to be ideally fulfilled in nickel zinc ferrite. A solution containing the ions *Ni* and *Zn* in the 15 : 35 and containing proportion somewhat less than 50 percent of iron, on precipitation and sintering at temperatures as low as 1000 and 1100° C, leads to a product, which has μ_0 near 100 and a good h.f. characteristic up till 10 M.C. Table XI gives some data observed on a sample of this kind.

TABLE XI

Sample of ferroxcube 4

$\mu_0 = 82$	$d = 4.8$	$\sigma = 70$	$d_{th} = 5.32$	$\rho = 10^6$
$f(MC)\quad=$	0.5	1	5	10
$\tan \delta\ (\%) =$	0.5	0.7	0.9	1.8
$C_r\quad=$	3.8	5.4	6.9	13.8

(Specimen contained 46 mol % of Fe_2O_3).

The advantages of a slight shortage of Fe_2O_3 is evident: the formation of Fe_3O_4 at high temperatures is counteracted; the surplus of NiO and ZnO provides the necessary strain.

On the other hand by making the proportion of the number of trivalent ions to the number of bivalent ions equal to unity, sintering at a higher temperature and cooling very slowly, exceptionally high values of μ_0 (with corresponding deterioration of the h.f. characteristic) can also be obtained with a nickel zinc ferrite. One particular sample had the properties mentioned in detail in Table XII.

TABLE XII

Nickel zinc ferrite 15/35/50

Heat treatment (oxygen):

1h. 1200°C + 2h. 1250°C + 7h. 1100°C + 33h. 1000°C + 34h. 950°Cs.c.

	B_0	A	B_0	A
$\mu_0 = 3.800$	129	0.12	1240	13
$\mu_m = 9.200$	390	1.6	1420	17
$H_e = 0.04$	680	4.2	1575	20
$\rho = 6.600$	1025	9.2	1680	20

A = Hysteresis loss in ergs per cycle.
B_0 = Maximum induction.

High μ-ferroxcubes are especially useful in chokes and transformers. It is evident however, that for $\mu_0 > 1000$ the care with which surfaces of air gaps have to be made flat, becomes unusually great. For many applications ferroxcube 1 with $\mu_0 > 1000$ is preferred to the high μ-variety of ferroxcube 4.
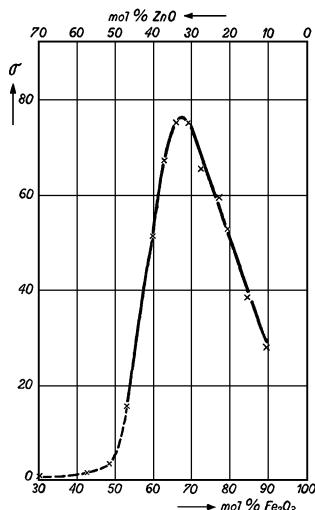

Fig. 33.
Saturation value of the magnetization for zinc ferrites of varying composition after prolonged sintering in oxygen at 1300° C. Samples containing Fe_2O_3 in excess have been partly dissociated.

§ 28. ZINC FERRITE

Conflicting statements are found in the literature about the magnetic properties of zinc ferrite [1]. In the view of the fact that in the foregoing we have always assumed zinc ferrite to be unmagnetic, while some authors have made statements to the contrary, a little explanation seems desirable.

The reaction between ZnO and Fe_2O_3 being very sluggish, only few of the specimens mentioned in literature may be assumed to have been homogeneous. It seemed desirable to study the properties of the whole binary system $ZnO - Fe_2O_3$.

Samples containing ZnO and Fe_2O_3 in varying amounts were ground very finely, pressed and sintered in oxygen at 1300°C. Only after 9 hours of sintering, substantially constant results were obtained. Fig. 33 shows that the saturation value has a maximum of about 78 at 70 mol % of Fe_2O_3 and is prac-

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[1] WOLOGDINE, C. R. Paris, **148** (1909) 776, ($T_c = 60°$ C).
S. HILPERT AND A. WILLE, Z. Phys. Chem. B, **18** (1932) 300, ($T_c = 70-80°$ C). MLLE SERRES, Diss. Paris 1931 (unmagnetic p. 54). Cf. Ann. de Phys., **17** (1932) 5. H. FORESTIER AND MLLE MARCELLE VETTER, C. R. Paris, **209** (1939) 164 (unmagnetic).

tically zero at the 50/50 ratio. Chemical analysis and measure-
ments of the specific electric resistance however show that
the samples contain Fe_3O_4.

On prolonged heating at 1000°C ferromagnetism disappears
in the whole binary system. This is partly due to reoxidation,
partly to segregation of the excess of Fe_2O_3. Fig. 34 shows two
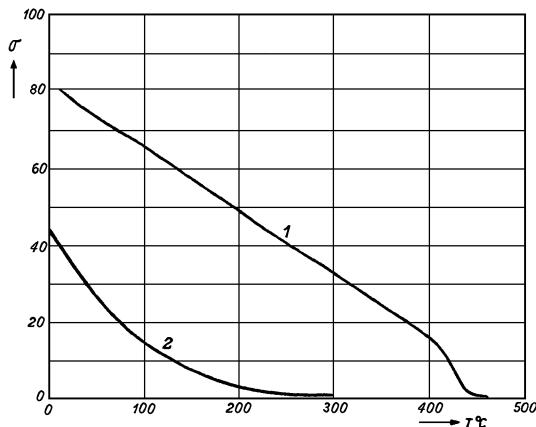
Fig. 34.
Curves showing the variation of σ with T of a zinc ferrite 30/70 very finely
ground and sintered in oxygen
a. heated at and quenched from 1300° C (Curve 1).
b. heated at and quenched from 1100° C (Curve 2).

σ-curves for the 30/70 ratio, one for a sample heated in oxygen
at 1300°C and containing a little Fe_3O_4, the other heated at
1100°C. The latter specimen contains no Fe_3O_4. It seems there-
fore that under very special conditions zinc ferrite containing
Fe_2O_3 in excess can be made ferromagnetic. The 50/50 ferrite
however is decidedly unmagnetic.

§ 29. *Fe-Al*-MAGNET STEEL

For a long time the old magnet steels, though having
only a $(B.H.)_{max}$ of about 0.3×10^6, have been unsurpassed
for their low cost of production. It is known that the addition
of cobalt to the steel, though leading to a substantial increase

in $(B.H.)_{max}$ causes the price to rise so much, that for many applications the carbon steels based on chromium or tungsten were preferred.

The discovery of the *Fe-Ni-Al* steels presented the original attack on this position, a $(B.H.)_{max}$ of 1 to 1.2×10^6 being attainable at the cost only of about 25% of nickel. The lack of malleability proved to be no serious obstacle for the wide-spread use of this material. Then came — after long unsuccessful attempts to make a better and at the same time not too costly steel — the *Fe-Co-Ni-Al* steels, which are heat-treated in a magnetic field (cf. the next section). They yielded — at the cost, it is true, of considerable amounts of cobalt and nickel — a $(B.H.)_{max}$ of 3.8×10^6 in manufacture (in laboratory 5.2×10^6) and they represent — besides magnet steels of previously unknown high magnetic power — alloys which allow the production of "magnetic energy" at a cost comparable to the cost involved in the manufacture of the old carbon steels. This high-quality steel, which was discovered by B. JONAS in this laboratory is therefore of double importance. There always remained however the need of a magnet steel of intermediate quality, say with about double the magnetic power of the carbon steels, which can be produced at low cost.

The magnet steels based on *Fe-Al-C* to be discussed here satisfy these demands and are therefore of first rate importance in the class of "low power magnet steels". They were developed in this laboratory during the war and have led to a magnetic power of 0.7×10^6. In the light of the foregoing facts it will be clear that the advantage obtained over the older carbon steels is important.

We shall not describe here at length the experiments leading to the optimum values for $(B.H.)_{max}$, but only say a few words about the ternary system *Fe-Al-C* in connection with the mechanism of hardening.

Steels containing approximately 8% *Al* and 1.5% *C* are among the best in the ternary system *Fe-Al-C* from a point of view of magnetic hardness. Our research has shown that at high temperatures alloys of this type are homogeneous and have a cubic face centered structure. This structure separates

into two isomorphous structures on cooling, much in the same way as happens in the case of *Fe-Ni-Al* to the cubic body centered phase. This is shown by the *X*-ray photographs. Crystals of one phase are found to have the same orientation as those of the other phase.

One of these face centered phases is the well-known γ-phase, the other has a superstructure and is called the ε-phase by F. R. MORRAL [1].

It was described by MORRAL as being mainly $Fe_3Al + 4\%$ of carbon. MORRAL considers the ε-phase to be ferromagnetic; we found this however to be only partly true. The ε-phase separating from alloys containing about 8% *Al* according to our findings is unmagnetic. Only for higher aluminium concentrations is the ε-phase magnetic, as shown by Fig. 35, where the Curie-temperature of the ε-phase is plotted against the aluminium content.

Fig. 35.
The variation of the Curie temperature of the ϵ-phase with aluminium content.

The ε-phase thus is not a uniform compound, but may have various compositions depending on the composition of the cast.

In alloys containing more than 10% aluminium only the α-phase (the well-known cubic body centered structure) appears besides the ε-phase. The coercive force in this region is quite small and so this type of alloy is hardly of interest to us. Below 10% aluminium, where as we have said magnetic hardness develops, an originally homogeneous cubic face centered phase on cooling separates into $\gamma + \varepsilon$. On further cooling γ transforms into $\alpha + \varepsilon$ again, thus yielding a magnetic product of com-

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[1] F. R. MORRAL, *J. Iron Steel Inst.*, **130** (1934) 419.

paratively high magnetic hardness. At low temperatures martensite may also be found.

The best results are obtained, if the material is first hardened at such a rate as to obtain a separation between γ and ε corresponding to an equilibrium at about $1000°$ C, as can be judged from the values of the lattice constants. The α-phase then has had only little opportunity to develop; but though the alloy is therefore only weakly magnetic, it proves to be very hard ($H_c > 400$ Oersted).

By annealing at a suitably chosen temperature (about $300°$C) γ is made to transform into α and the alloy becomes strongly ferromagnetic, H_c falling to 300 or 200 Oersted.

The hardening mechanism thus seems to be different from the mechanism found in $Fe\text{-}Ni\text{-}Al$ steels only in one respect. The first hardening product happens to be non-magnetic and has to be transformed into a ferromagnetic phase after hardening, the latter process causing a slight reduction in H_c.

Table XIII gives some data of lattice constants measured on both face centered phases at various temperatures and in the hardened condition.

TABLE XIII

Temperature of quenching	a_ϵ	a_γ		a_ϵ	a_γ
1200° C	3.660				
1000	3.756	3.648			
900	3.771	3.648	Cooled in 15 sec. from 1200° C	3.712	3.643
800	3.760	3.639			
700	3.779	3.640			
500	3.780	3.618			

§ 30. *Fe-Co-Ni-Al* MAGNET STEEL

About the mode of manufacture and the performance of the magnet cooled steel sufficient material has already been

published [1], which need not be repeated here. We only wish to discuss here the mechanism by which the excellent magnetic properties are brought about.

In a nutshell the situation is this: cubic body centered alloys of *Fe-Ni-Al*, to which so much cobalt has been added, that the Curie temperature and the saturation value are increased as much as possible, on cooling in a magnetic field prove to develop a magnetic anisotropy of a "well-behaved" kind instead of the irregular magnetic anisotropy leading to a quasi isotropic behaviour of the well known-type.

At the same time we must assume that much of the "irregular" character must have remained, otherwise the alloy would have been magnetically anisotropic, but not magnetically hard.

From a theoretical point of view it would have been satisfactory to note a simultaneous rise in the remanence along with a corresponding decrease in the coercive force. In the technically important alloys such a decrease is not observed.

It may at once be added however that a *Fe-Co-Ni-Al* alloy to which some silicon (0.75%) had been added, was found to combine an exceptionally high value of the remanence with a relatively low value of H_c. It thus seems that current theory, which predicts a relatively low coercive force for samples which are anisotropic but otherwise homogeneous, is not to be distrusted and that the new alloys merely represent a very good compromise between two conflicting conditions.

The chief question to be answered remains: how and by what means does the magnetic field operate on the alloy during cooling in such a way, that the final result of the hardening is changed so drastically?

Attempts were made to obtain further insight into the problem by changing the experimental conditions: if the orientation of the spins is the only thing that matters, why not make them

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[1] G. HOLST, *Hand. Nat. Gen. Congres* 1939 p. 19; J. L. SNOEK, *Phil. techn. Rev.*, **5** (1940) 195. A. TH. VAN URK, *Phil. Techn. Rev.*, **5** (1940) 29; B. JONAS AND H. J. MEERKAMP VAN EMBDEN, *Phil. techn. Rev.*, **6** (1941) 8; J. F. KAISER, *Engineer*, 170 (1940) 183; A. PORTEVIN, *Journ. Phys. Rad.*, **4** (1943) 17.

choose position by applying an external pressure during cooling? Experiments proved to be difficult and the result wholly negative, as the effect sought for was covered by a much larger effect: magnetic hardness is getting lost at an appalling rate by mechanically interfering with the sample during cooling. The observed strong decrease in H_c might be ascribed to plastic deformation. To us however this seems highly improbable in view of the fact that the specimen had hardly changed as a result of the applied stress. Instead of solving the problem, we have therefore added one to the series.

No unanimity of opinion yet exists as to the composition of the unmagnetic a-component making its appearance in alloys of the *Fe-Ni-Al* type at low temperatures; the author holds the view that this composition is nearly identical with $NiAl$ [1].

In the following description we will keep to the convention that this unmagnetic component is indeed $NiAl$, though it is not essential to our discussion. In former experiments on Fe_2NiAl we have shown that the unmagnetic component makes itself known by its demagnetizing action and does so especially strongly in alloys which are heat-treated so as to develop maximum magnetic power.

It is natural to suppose that in alloys of a related type, in which by the addition of cobalt the Curie temperature has been increased as much as possible, the demagnetizing action of the unmagnetic "germs" will play a part in the history of their growth and development.

Ferromagnetic "germs" in unmagnetic or weakly magnetic surroundings will grow faster in one direction than in the two others, if placed in a magnetic field. Unmagnetic inclusions in magnetic surroundings will also have the tendency to grow stronger in the direction of the magnetization than in other directions.

If this is true, part of the apparent inner demagnetization observed in the magnet hardened specimen would really be due to demagnetization effects. Part of the observed anisotropy must however be "real", otherwise no magnetic hardness

[1] J. L. SNOEK, *Physica*, **6** (1939) 321.

would be found. Keeping the above picture in mind, a test would be obtained if one succeeded in proving that the magnetic saturation was smaller when measured in the direction of "preferred" magnetization than in a transverse direction, an "air gap" reducing the saturation only when placed parallel to the material.

Experiments carried out with a view to verifying this contention, led to no decisive result. In view of the smallness of the effect to be expected this is not surprising. Even if the whole of the observed anisotropy were due to demagnetization the effect would be quite small (about 2 %). The true magnitude of the inner demagnetization can be found by measurements on quasi isotropic samples, as the effects of the various stresses on the magnetization curve cancel each other here, leaving only the inner demagnetization active. It proved to be quite small in the alloys which show the anisotropy effect.

It is highly probable, therefore, that these alloys split up into two ferromagnetic components. One will of course be much more weakly magnetic than the other. For such alloys our demagnetization theory would be just as applicable as for alloys which contain an unmagnetic component. Moreover it is to be kept in mind that the question "magnetic or unmagnetic" has to be answered in reality at the temperature of hardening.

All things considered there seems to be no reason to doubt our theory of anisotropic hardening, but the means of effectively testing it seem to fail so far.

THE INCLUSION MODEL OF FERROMAGNETIC HYSTERESIS

The inclusion model of ferromagnetic hysteresis starts from the consideration that any boundary layer which is the seat of a surface energy will have the tendency to contract itself like the surface of a soap bubble or of a drop of water. It is further observed that unmagnetic inclusions when forming part of a Bloch boundary layer, reduce the active surface of that layer. The fundamental equation (5) is arrived at as follows: a displacement of a Bloch zone by an amount dx causes the energy per cm^2 to decrease by an amount $-H \cdot I_{max} \cdot dx$, if the cosine of the angle φ enclosed by the spins and the field is thereby changed from 0 to 1 (Fig. 1). Equilibrium conditions are reached if this energy is balanced by the increase $\gamma \cdot \dfrac{1}{O} \cdot \dfrac{dO}{dx}$ of the surface energy per cm^2.

A plane cutting the small spheres of Fig. 1, representing the inclusions, at a distance x from the equatorial plane has an active surface O equal to

$$O = s^2 - \pi \left(\frac{d^2}{4} - x^2 \right) \tag{91}$$

per total surface s^2. From this we find that

$$\frac{1}{O} \cdot \frac{dO}{dx} = 2\pi \frac{x}{s^2}$$

or

$$H = \frac{\gamma}{I_{max}} \frac{1}{O} \cdot \frac{dO}{dx} = \frac{\gamma}{I_{max}} \cdot 2\pi \cdot \frac{x}{s^2} \cdot \tag{92}$$

If x reaches the critical value

$$x = \frac{d}{2},\qquad(93)$$

the increase in the active surface suddenly comes to an end and a ''jump'' or discontinuity in the magnetization takes place. The critical field H_0 is therefore equal to

$$H_0 = \frac{\gamma}{I_{max}} \cdot \pi \frac{d}{s^2}\qquad(6)$$

The initial susceptibility χ_0 is defined as

$$\chi_0 = \frac{\mathrm{d}I}{\mathrm{d}H} = \frac{\mathrm{d}I}{\mathrm{d}x} : \frac{\mathrm{d}H}{\mathrm{d}x}.\qquad(94)$$

From (92) we find, that $\dfrac{\mathrm{d}H}{\mathrm{d}x}$ for $H < H_0$ is a constant and equal to

$$\frac{\mathrm{d}H}{\mathrm{d}x} = \frac{2\pi\gamma}{s^2 I_{max}}.\qquad(95)$$

It is further easily seen, that $\dfrac{\mathrm{d}I}{I_{max}}$ is equal to $\dfrac{\mathrm{d}x}{s}$, if every potential minimum is occupied by a Bloch zone, and to $\beta\dfrac{\mathrm{d}x}{s}$ if only a fraction β of these minima actually is occupied. We thus find for χ_0

$$\chi_0 = \frac{\beta \cdot I_{max}}{s} : \frac{2\,\pi\gamma}{s^2 \cdot I_{max}} = \frac{\beta}{2} \cdot \frac{s}{\pi} \cdot \frac{I^2_{max}}{\gamma}\ (7),\ \text{q.e.d.}$$

THE INFLUENCE OF EDDY CURRENTS ON THE APPARENT HYSTERESIS LOOP OF FERROMAGNETIC BARS

by J. L. Snoek

1. *Introduction.* In the course of a research on certain magnetically very weak materials, which were examined in the form of straight bars, it was found, that the rate of change of the magnetizing current materially affects the form of the hysteresis loop. As the publications on the subject are very scarce and very old, we decided to look somewhat deeper into the subject.

After due time an explanation was found, which covered all the known facts. As this explanation — as far as we know — is new, we shall bring it here, together with some experimental evidence, supporting it.

We shall show in the next paragraph that if the magnetizing current is varied so rapidly that it causes an appreciable lagging behind of the magnetization in the interior part of the bar with regard to the outer part, the measured mean induction in the bar will differ considerably from the one obtained after a sufficiently slow variation of the field. The effect is expected to occur only on open magnetic circuits, i.e., on bars, wires, ellipsoids, and the like.

As a matter of fact on ring samples no influence at all of the rate of change of the magnetizing current upon the hysteresis loop was detected.

We will show in the third section, that in extreme cases the measured value of the coercive force may be in error by a factor two or more. The error in the total hysteresis loss is still larger. It will further be shown that the newly identified source of errors has given rise to a considerable number of inconsistencies and controversies in the past, the cause of which is now explained.

Amongst them is the curious fact, sometimes mentioned but more often ignored in publications, that the normal induction curve lies partly outside of the main loop. (The normal induction curve is the curve starting from the demagnetized state).

This anomaly appears to be only the outcome of errors in the measurement due to a too rapid magnetization of the bar. In ring samples it does not occur.

2. *Explanation of the eddy current effect*. We rather regret being unable to give the explanation in quantitative terms. A quantitative formulation would involve cumbersome calculations and seems hardly worth while.

The process of shearing back, by which the true hysteresis curve of a material is found from the apparent one, as measured on a bar (or better on an ellipsoid) is almost too well known to be mentioned here. However fundamental as it is to our explanation, we will indicate it briefly. If D is the demagnetizing coefficient, a function of the shape of the specimen, H_i the internal field, H_e the external field and I the magnetization of the bar, than it is well known [1] that H_i and H_e are related by the equation:

$$H_i = H_e - D \cdot I. \tag{1}$$

From this follows the equally simple relation:

$$\varDelta H_i = \varDelta H_e - D \cdot \varDelta I. \tag{2}$$

which applies to an arbitrary change in the external conditions. This equation forms the basis of our explanation.

From (2) it seems to follow that if a rapid change in H_e is brought about, for a very short time the internal field may be much larger than its final value, due to the fact that the term $D \varDelta I$ not immediately reaches its final value.

This of course is not wholly true. The fact, that immediately after the change in H_e a change in the magnetization I sets in, implies, that eddy currents are set up in the sample, temporarily shielding the interior part of the bar.

The outer part of the bar — and that is the vital point in

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[1] *Handbuch der Physik*, Berlin 1927, p. 102, 111 and 168.

our explanation — is not shielded off and therefore for a while is exposed to a much higher field than corresponds with the final state. This means, *that the outer part of the bar after the change in the external field does not find itself on the ascending limb of the loop, but on some descending limb.*
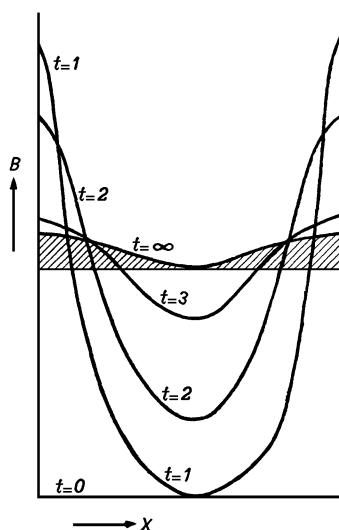

Fig. 36.

Diagram of the variation of the magnetization over the cross section of a bar in the course of time after a sudden change in the external field In the middle part the magnetization rises asymtotically to the final value. The outer parts for a short time assume a much higher magnetization and then gradually fall back to a final value, which lies higher however than agrees with the ascending limb of the loop.

The effect is largest in the "knee" of the ascending limb because there the term $D . \Delta I$ is largest with regard to the term ΔH_i. This is, what is found experimentally. However, as we shall show, in extreme cases the whole of the hysteresis loop is seriously affected if the magnetizing current is varied too rapidly.

The eddy current effect depicted above is no doubt a little difficult to visualize. We shall therefore put it in another way. One may say, that due to the shielding action of the eddy current, the demagnetizing coefficient D is temporarily diminished. For a short while the specimen acts as if it were a hollow tube instead of a massive bar. Now a diminution in the demagnetizing coefficient of course results in a temporary increase in the effective field strength and so in a temporary magnetization, which temporary is too high.

Fig. 36 represents the way the magnetization varies over the cross section of the bar during magnetization.

We shall illustrate the effect by a series of measurements on specimens, specially selected for the purpose. In these

measurements the magnetizing current was first changed so slowly and continuously that hardly any eddy currents were set up in the material. The results obtained in this way were found to be mutually consistent.

Then the hysteresis loop was measured again in the old careless way by simply switching the magnetizing current on and off. Care was taken however, that no oscillations in the magnetizing current occurred during operation of the circuit. The resulting curves are compared with the true values.

The same was done for the normal induction curve. This comparison leads to a natural explanation of a very annoying discrepancy, observed in the past on this curve.

3. *Choice and preparation of the specimens.* As mentioned above, ring samples do not show the effect. We shall not therefore reproduce here any of our measurements on rings.
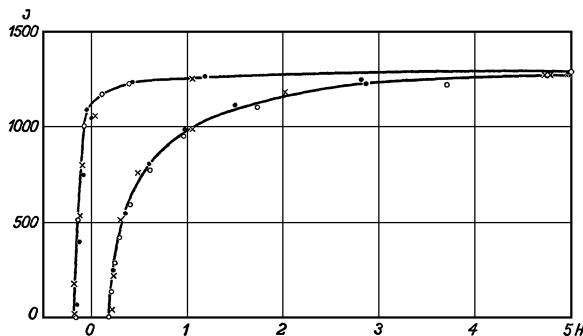

Fig. 37.

Points on the main loop of three samples cut from the same stock but of widely differing dimension ratio.

Open circles: No. 1; dimension ratio $r = 469$; demagnetizing factor $D = 0.00026$.
Black dots: sample No. 2; $r = 151$; $D = 0.0025$.
Crosses: sample No. 3; $r = 51$; $D = 0.0153$.

A bar of carbonyl iron was drawn into a wire of 1 mm diameter and then cut into three pieces of widely differing lengths (about 45, 15 and 4 cm). These samples were annealed under such conditions as to ensure an identical and homo-

geneous internal condition, complete absence of magnetic after effect and a high permeability.

Ballistic measurements were made on these three samples in the following way: the magnetizing current was brought slowly and continuously to the required value by means of sliding resistances. Then the sample was drawn out of the test coil and the throw of the galvanometer observed. Care was taken that the wire was not damaged during removal from the
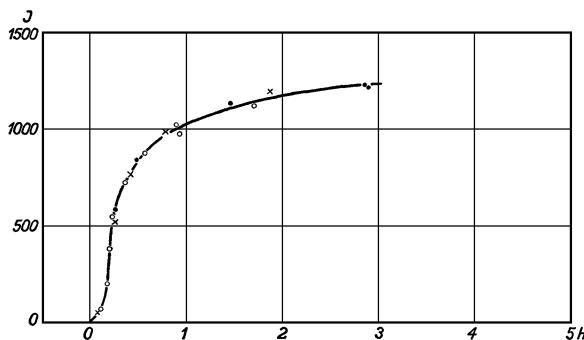

Fig. 38.
Points on the normal induction curve of the samples Nos. 1, 2 and 3. Same notation as in Fig. 37.

test coil. For each point, of course, the whole process had to be repeated. The curves obtained in this way could be accurately reproduced. The measured curves were sheared back in the known way and the resulting loops compared. For the two shorter samples the demagnetizing coefficient had to be slightly adjusted (less than 1%). To our satisfaction the three curves obtained in this way were very nearly identical, pointing to a good homogenety of the material. (The near identity of the three curves was of course by no means vital to our ends, but it makes the mutual comparison of results obtained in another way a much more elegant affair). Fig. 37 gives all the measured points for the main loop. Fig. 38 shows the points measured for the normal induction curve. Here also the mutual agreement is satisfactory.

In Fig. 39 the main loop and the normal induction curve
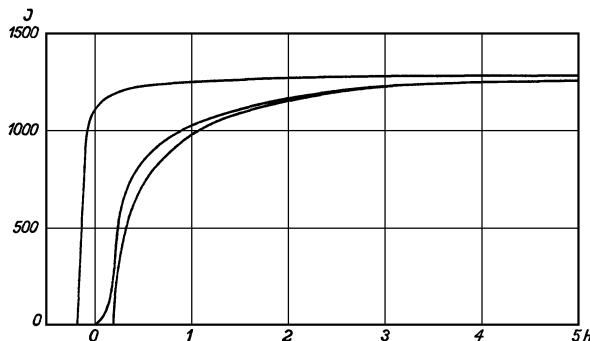
Fig. 39

The main loop and the normal induction curve of samples Nos. 1, 2 and 3, superimposed. The latter lies well within the former.

are shown superimposed. It is seen that the latter falls well inside the former.

4. *Effect of a too rapid change of the magnetizing current.* Before discussing experiments, in which the current was changed more rapidly, the exact meaning of the terms "rapid" and "slow" must be discussed. The time constant of the sample will be named τ, that of the magnetizing current τ^*. It is evident that "rapid" means $\tau^* \gg \tau$ and "slow" $\tau^* \gg \tau$.

Eddy current theory tells us, that the time τ required by the specimen to adapt its magnetic state to that of its surroundings is roughly equal to the reciprocal of the frequency at which magnetic skin effect sets in [1]. This latter frequency is given by the equation

$$\frac{8\pi^2 f \mu a^2}{\varrho \cdot 10^9} \sim 1 \tag{3}$$

where μ is the permeability, a the diameter and ϱ the specific

[1] B. and D. p. 230.

electric resistance of the bar. This leads to the following value
for τ with $a = 1$ mm and $\varrho = 10^{-5}$ ohm.cm.

$$\tau \sim \frac{8\pi^2 f \mu a^2}{\varrho \cdot 10^9} \sim 0{,}0001\,\mu \qquad (4)$$

μ is of course variable but for our sample larger than 1000
throughout. From (4) it is seen, that a careful manipulation
of the sliding resistances will lead to a variation of the magneti-
zing current which is sufficiently slow to produce no measurable
retarding of the magnetization except perhaps on the steepest
parts of the loop.

The time τ^* required for the field inside a magnetizing coil
to build up or disappear, when the current is switched on and
off in the usual way, will of course depend upon the impedances
present in the circuit under the conditions of the measurement.
It will therefore be variable even in the course of one expe-
riment. In general however τ^* will be smaller than τ, if the
material under investigation has a high permeability.

In our arrangement, where we made use of a battery giving
50 volt and of a long coil wound in 8 consecutive layers, the
time τ^* varied between 10^{-3} and 10^{-6} sec. We made certain
by means of the cathode ray-oscillograph that no oscillations
occurred while operating the circuit.

From the above we may conclude that in the experiments
now to be described the magnetizing current was varied so
rapidly that it caused in the sample about the maximum
time lag possible between the magnetization and the field.

On the other hand for samples with a high coercive force
($H_c > 100$) the permeability μ will be so much lower and the
self induction of the coil so much higher, that for these cases
τ^* will soon exceed τ. Therefore no eddy current effect is to
be expected for materials, which are magnetically hard.

The results of the measurements of the mainloop on specimens
No. 1, 2 and 3 are shown in Fig. 40, 41 and 42 (dotted lines)
superimposed on the true hysteresis loop. The deviations from
the true form are seen to depend strongly on the dimension
ratio, as expected, and for the shorter specimens No. 2 and 3
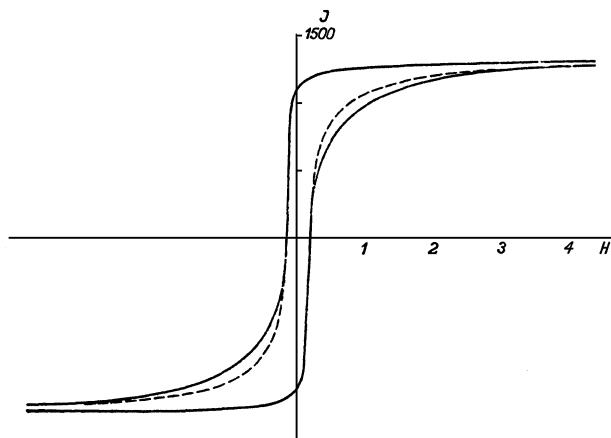
Fig. 40.
Main loop of sample No. 1 measured in two different ways.
Drawn line: true hysteresis loop. Dotted line: deviation due to
the sudden change of the external field.
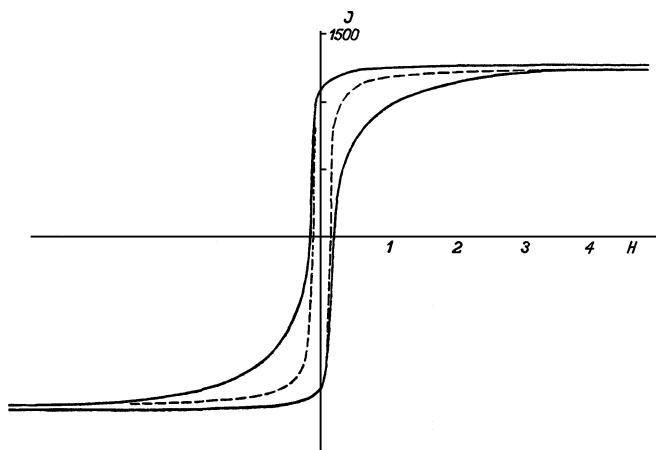
Fig. 41.
Main loop of sample No. 2 (cf. Fig. 40.)
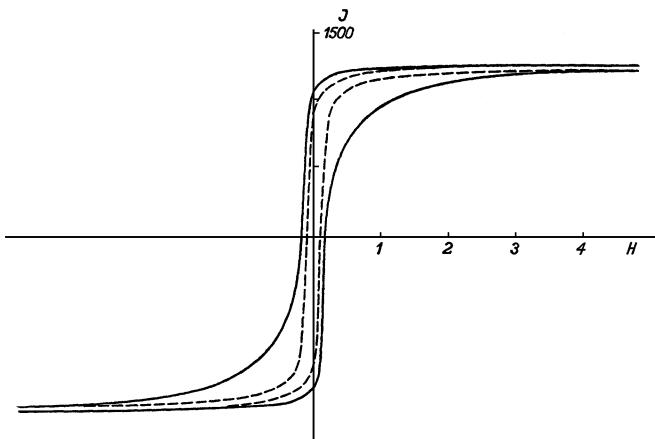
Fig. 42.
Main loop of sample No. 3 (cf. Fig. 41).

are quite considerable. Even for specimen No. 1 however,
which has only a very small demagnetizing coefficient
($D = 0,00026$) the difference is not negligible.

In specimen No. 3 the error committed in the hysteresis
loss is evidently enormous. Even the coercive force is at fault
by a factor 2, although as can be seen from specimen No. 1,
the latter is not nearly so sensitive to this source of errors
as the induction in the "knee".

5. *The normal induction curve.* THOMAS SPOONER[1]-in his
textbook on "properties and testing of magnetic materials"
remarks, that from time to time the normal induction curve
fails to lie inside the main loop. "This is more often the case
than not, although textbooks generally show the curve well
inside the loop. Apparently no satisfactory explanation of
this effect has been published". From a search of the older
publications on the subject two facts become clear:

1. The effect has been observed on bars only.

2. The normal induction curve used to be measured in

[1] THOMAS SPOONER, ,,*Properties and testing of magnetic materials*".
New York—London 1937, p. 18.

consecutive little steps ("step by step method"), which were
then added.
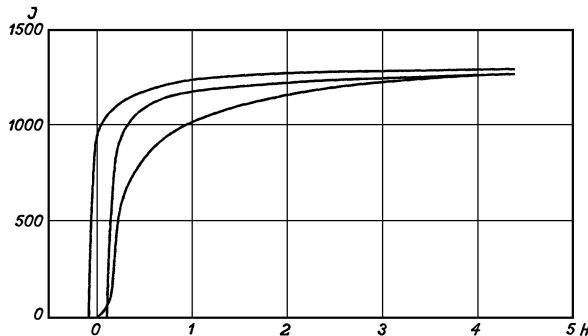
Fig. 43.

Main loop of sample No. 3, as measured by switching on and off the current
in the usual way and normal induction curve as measured after slowly and
continuously varying the current. The latter procedure is approached by the
,,step by step" method, in which the current is increased in small steps.

Now the "step by step" method so nearly equals a continuous
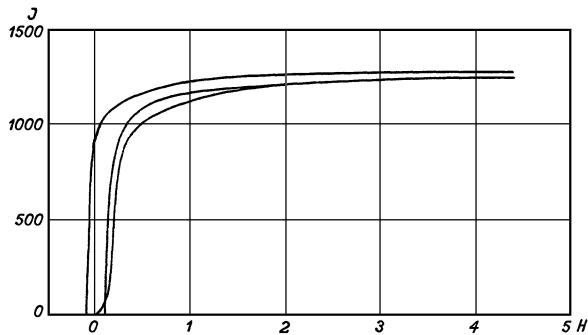
Fig. 44.

Main loop of sample No. 3 and the normal induction curve both measured
in the same erroneous way. Here as in Fig. 43 the curve lies partly outside
the main loop, though the effect is less striking.

variation of the magnetizing current, that it is worth while
comparing the normal induction curve obtained in this way

with the main loop as measured by the ordinary method.

This has been done in Fig. 43 for specimen No. 3.

The picture obtained is clearly satisfactory in that indeed the curve stretches well out of the loop.

We need not go quite as far as that however, in order to explain the anomalies obtained in the past.

Fig. 44 shows the main loop and the normal induction curve of specimen No. 3 superimposed, both being measured by the ordinary method of switching on and off the current.
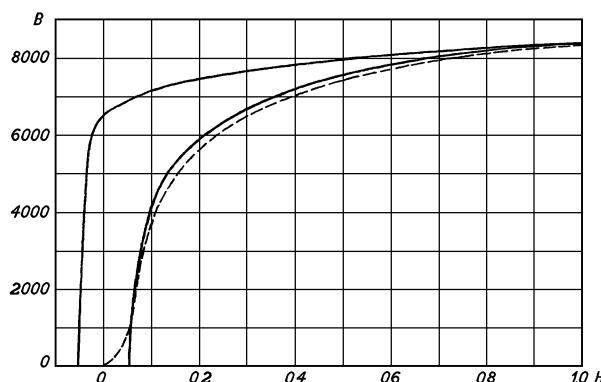

Fig. 45.
Reproduction of the main loop and the normal induction curve as obtained by P. P. CIOFFI on a permalloy wire [1]. As in Fig 9 the normal induction curve lies partly outside of the main loop. The induction was measured by switching the current off and on.

Though the effect is less pronounced, yet the curve lies again partly outside the loop.

The explanation of this fact is that the term $D \Delta I$, which is responsible for the error, is larger for the main loop than for the normal induction curve by at least a factor two.

How utterly unknown the above described eddy current effect is to present workers in the field, is indicated by Fig.45, which is a reproduction of data given by P. P. CIOFFI [1] in a paper, specially dealing with the technique of measuring the

[1] P. P. CIOFFI, *J. opt. Soc. Amer.*, **9** (1924) 53.

magnetic properties of magnetically soft materials in the form
of long wires. In this figure the main loop and the normal
induction curve as measured by CIOFFI on the same specimen
(a permalloy wire of 1 mm diameter) are shown superimposed.
The normal induction curve clearly lies outside the main
loop.

The dimension ratio of this wire was so large (about 600)
and the demagnetizing factor so small (about 10^{-5}) that the
author did not even take the trouble of correcting his curves
for this shearing action. Yet from the curves, as well as from
further data supplied by the author on the measuring technique
it can be concluded with certainty that, due to the eddy current
effect, the induction in the "knee" was measured too high
by at least ten per cent.

6. *Other inconsistencies*. From the foregoing it is evident
that all measurements made in the past on magnetically
weak materials in the form of bars or ellipsoids are to be
distrusted. Especially the hysteresis loss and to a less extent
also the coercive force may have been underestimated in
many cases. This perhaps accounts for the fact that some
makers of a very pure iron were disappointed to find that the
coercive force of their samples was not quite so low as might
have been expected from data obtained by others on less
pure specimens. The latter data probably were too low.

Another point, which has been much discussed in the past,
is the so-called "WALTENHOFEN phenomenon" [1]. The value
of the apparent (= unsheared) remanence is found to depend
on the field strength employed in saturating the sample. In
general the stronger this field, the lower the remanence.
Even reversals of the sign have been observed. We have
sought for a WALTENHOFEN effect in ring samples, but
found none at all. On the other hand we have shown, that
on samples in the form of a bar a decrease of the remanence
with increasing saturating current may be observed due to

[1] J. L. GRAETZ, *Handbuch der Elektrizität und Magnetismus I V*,
Leipzig 1920, p. 334.

an increasing eddy current, thus leading to an effect of the kind considered.

The retardation required in the magnetizing current in order to obtain correct data, is not large. The insertion of a metallic non magnetic tube between the sample and the coil is for most cases sufficient.

As a matter of fact this was the way in which the effect was discovered, a coil with a water cooled core yielding results which were persistently different from those obtained on other coils.

An influence of inserting a metal tube inside the magnetizing coil has been observed before by B. O. PEIRCE [1], but evidently the effect was not correctly interpreted.

APPENDIX III

Reprint from Physica VIII, no. 7.

ON THE DECARBURIZATION OF STEEL AND RELATED QUESTIONS

by J. L. SNOEK

1. *Explanation of the formation of ferritic bands.* As is well known surface decarburization of steel is most effectively done by heat treating the sample for several hours in hydrogen moistened with water vapour at a temperature lying between 700° and 800° C.

In this note we propose to deal with the mechanism of this decarburization process as well as with certain other questions concerning the influence of carbon on the properties of iron.

Figs 46 – 49 show on more details of the decarburization process. They have been taken from a paper by D. H. ROWLAND

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[1] B. O. PEIRCE, *Proc. Amer. Ac.*, **47** (1912) 633; Contr. Jefferson Lab. Harvard, 1911, No. 8.

and CLAIR UPTHEGROVE [1] on the subject and rearranged in order to emphasize some features more properly.

Fig. 46 shows a cross sectional microphotograph of a steel containing 0.7% carbon, which had been heat treated for 50 hours at 790°C. On the same scale is plotted a graph denoting
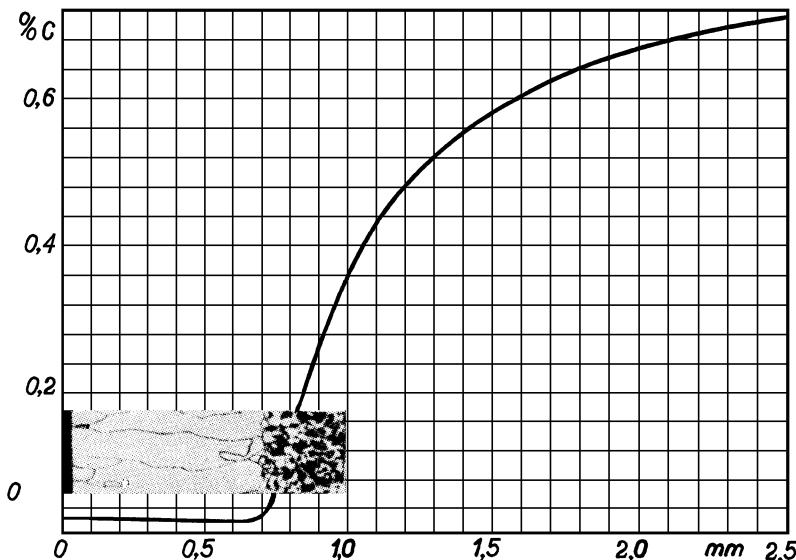
Fig. 46.

Microphotograph of steel decarburized for 50 hours at 790°C in hydrogen saturated with water vapour. × 100. The diagram gives the carbon content in consecutive layers as determined by chemical analysis of peripheral turnings from the test rod.

the carbon content as a function of the depth under the surface. This diagram and more strikingly even the microphotograph show the existence of a nearly completely decarburized surface layer, below which the carbon content rises steeply to much larger values.

[1] D. H. ROWLAND AND CLAIR UPTHEGROVE, *Trans. Am. Soc. Met.*, **24** (1936) 96.

We are interested in the way in which this ferritic band comes into existence.

Fig. 47 gives microphotographs of the same steel after heat treatment for 5, 20 and 50 hours respectively at a somewhat lower temperature (735° C). The boundary is even more sharp
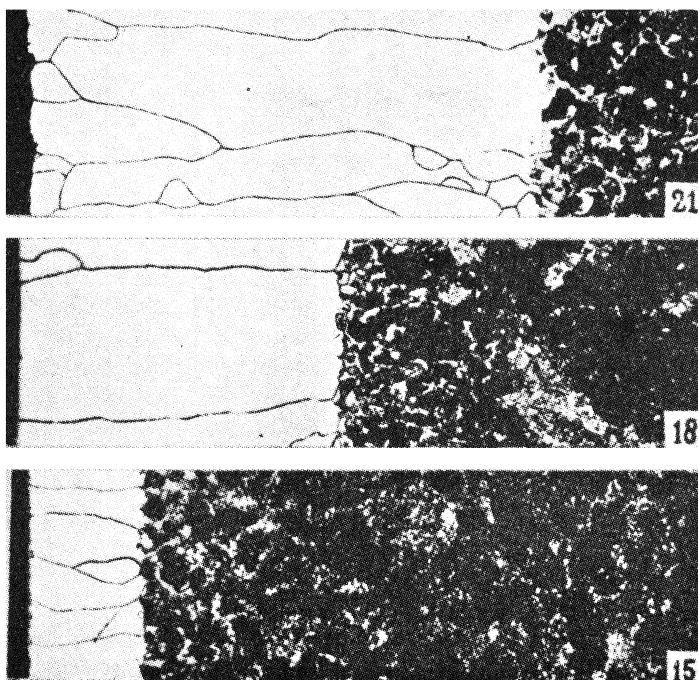
Fig. 47.
Steel decarburized for 5, 20 and 50 hours respectively at 735° C in hydrogen saturated with water vapour. × 90.

here and is seen to displace itself gradually in the course of the heat treatment.

In Fig. 48 the displacement of the boundary has been plotted against time.

The diagram of Fig. 49 finally shows the depth reached after 50 hours at various temperatures of the decarburization.
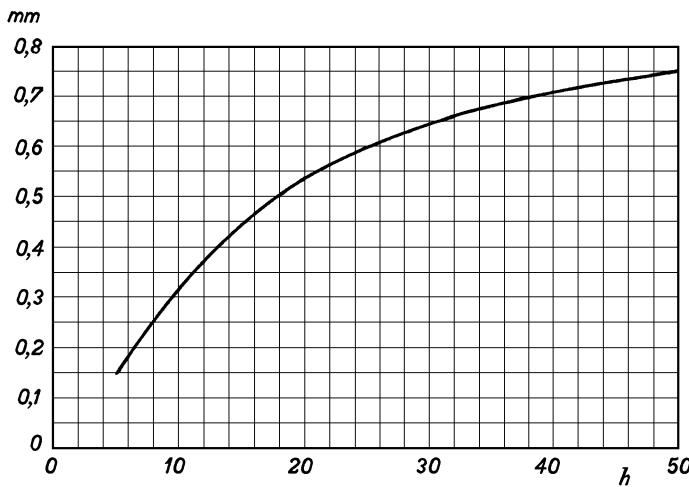
Fig. 48.
Relation of the width of the ferrite band to time at 735° C.
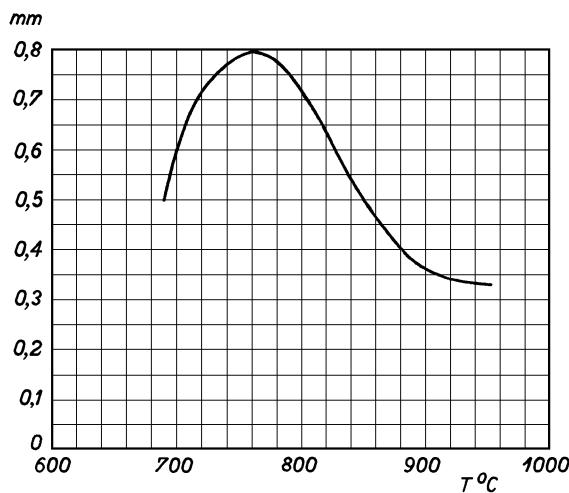
Fig. 49.
Effect of temperature on width of ferrite band.

A broad maximum is found near 760° C. Below 685° C and above 900° C no such ferritic bands are found.

Various attempts to explain this ferritic band have been made in the course of time, but so far without much success [1]. Fig. 50 gives the relevant portion of the iron carbon diagram. The upper limit of the temperature interval where ferritic bands are observed coincides more or less with the temperature above which no ferritic phase is present during heat treatment. Clearly the presence of such a phase during the treatment is essential for the occurrence of a decarburized zone with a sharp boundary.

In the course of some work on magnetic after effect in highly pure iron in which traces of carbon were present we arrived at the conclusion that the phenomena of after effect, which were clearly connected with the presence of such small traces of carbon in the iron, could only be explained by an act of diffusion of the carbon under the influence of a magneto-strictive strain [2].

The strong temperature dependence of the phenomenon made such a conclusion seem inevitable. Conversely this temperature dependence could be used for a determination of the activation energy characteristic of the diffusion process in the ferritic phase. Assuming that a formula of the general form

$$D_a = D_0\, e^{-A/T} \tag{1}$$

for the diffusion also holds in this case, it was found that A was equal to $9000\,°K$ for the α-phase.

For γ iron the most reliable determination of D gives: [3]

$$D_\gamma = 0.49\, e^{-18300/T} \tag{2}$$

It is at once seen that the rate of diffusion of the carbon

[1] Cf. W. BAUKLOH AND B. KNAPP, *Arch. Eisenhüttenw.*, **12** (1939) 405.

[2] J. L. SNOEK, *Physica*, **6** (1939) 161. Cf. also: B. and D., p. 262.

[3] W. JOST, *Diffusion und chemische Reaktion in festen Stoffen,* Dresden 1937.

in the α phase must be enormously much higher than in the γ-phase under otherwise comparable conditions. For the $\alpha - \gamma$ transition point one calculates for the ratio D_α / D_γ, assuming that the value of D_0 is the same for both phases.

$$\frac{D_\alpha}{D_\gamma} = e^{9300/1183} = 2600 \tag{3}$$
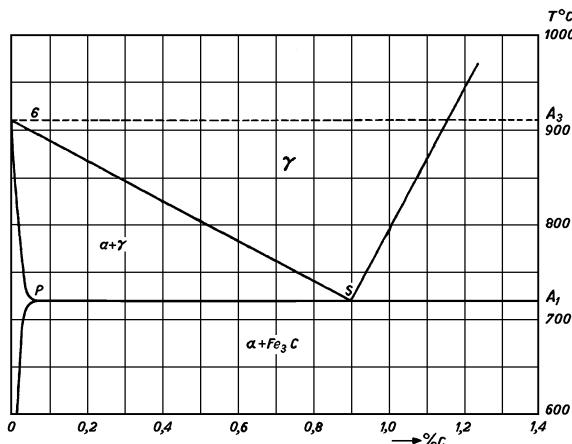
Fig. 50
Part of the iron carbon diagram.

This of course is a surprising conclusion [1], the current opinion being that the rate of diffusion of carbon in de α phase is much smaller than in the γ phase.

However from the evidence cited above about the occurrence of ferritic bands after decarburization, as well as from certain experiments of our own concerning the decarburization of low carbon alloys, it is seen that the discovery of this fact constitutes the finding of the missing link in the whole chain.

In fact once the fact is recognized that the rate of diffusion

[1] Later (1944) calculations by Dr D. POLDER of this laboratory have shown the coefficient D_0 to be equal to $0,52.10^{-3}$ for α iron thus reducing the factor 2600 to much more reasonable values.

of carbon in the α phase is unusually high, there is nothing mysterious any more in the occurrence of the characteristic ferritic bands under the circumstances given.

As may be seen from the iron carbon diagram (Fig. 50) in a certain temperature interval lying between A_1 (720°C) and A_3 (910°C), the carbon finds itself in solid solution in the γ-phase at the beginning of the decarburization process. Very soon however the surface becomes poorer in carbon content and the alloy then enters the two phase region GSP.

As soon as the α phase has been formed to such a degree as to establish sufficient connection between the individual regions, this phase acts as a perfect "drain" on the remaining carbon and therefore the surface layer soon becomes completely ferritic. In the course of the further decarburization the ferritic phase always remains immediately "on the track" of the newly formed two phase layer. This lasts until the ferritic layer has become so thick that the diffusion begins seriously to hamper the rapid removal of the carbon.

The maximum of Fig. 49 remains to be explained. The rapid falling off towards lower temperatures is a natural consequence of the decrease in the diffusion with temperature. On approaching A_3 there are other reasons for a decline of the rate of growth of the ferritic band. The first is that the critical concentration at which the γ phase disintegrates into $\gamma + \alpha$ becomes smaller with increasing temperature. Secondly the maximum solubility of carbon in the α phase decreases. Above A_3 no such characteristic ferritic bands are observed, although, of course part of the material turns into ferrite after cooling.

2. Other estimates of the rate of diffusion of carbon in the α phase. A direct determination of the rate of diffusion of carbon in the α phase would of course be desirable, but seems out of question because of the very small solubility. We have however other indirect evidence to cite besides the argument derived from the study of the after effect, which also lends strong support to the idea that the rate of diffusion in the α phase is exceedingly high.

It was observed, that an iron cobalt alloy of composition

50/50 in order to yield a high induction in a field of say 10 Oersted had to be heated in hydrogen for a long time. The time required proved to be a function of the diameter and so it was concluded that the magnetic quality of the alloy depended upon the degree of decarburization.

For this alloy the $\alpha - \gamma$ transition point lies at 980 °C. It occurred to us that a series of decarburizing treatments immediately below and immediately above the transition point would probably reveal the higher efficiency of a treatment
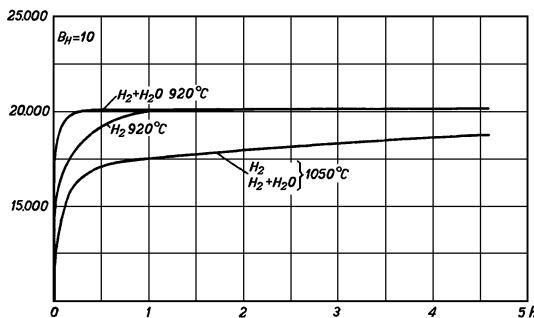
Fig. 51.

Effect of decarburizing treatment on the induction measured at $H = 10$ Oe for a 50/50 *Fe Co* alloy. Decarburizing was done slightly below and slightly above the $\alpha \to \gamma$ transition point (980 °C). Diameter of the specimen : 1.5 mm.

at the lower temperature on account of the reasons mentioned above. As the decarburizing agent dry hydrogen and hydrogen with water vapour was chosen. Fig. 51 shows the variation of $B_{H=10}$ as a result of a treatment in purified hydrogen. At 920 and at 1050°C respectively evidently the same final value is approached, but the time required at 1050°C is much longer. Of course the differences might have been concealed or exaggerated by differences in the velocity of the surface reaction. As the next step, water vapour was therefore introduced into the hydrogen. By this change the high temperature curve was not affected in the least, but the reaction at low temperatures now proved so fast that after 10 minutes the specimen, which had a diameter of 1.5 mm, was completely decarburized.

In our opinion this magnetic evidence proves conclusively

that a time of 10 minutes at 920 °C is amply sufficient for the carbon to cover a distance of 1 mm. This again is only possible if the coefficient of diffusion is indeed of the high magnitude anticipated by us.

3. *Affinity relations, value of the combustion test and maximum decarburization obtainable.* It was shown by us in earlier papers [1] that the presence of small quantities of carbon in solid solution in annealed iron not only leads to a magnetic after effect, but also that an elastic after effect is produced.

Carefully purified samples of iron show, when the internal damping is measured for a frequency in the neighbourhood of 1 per/sec between —50 and +50 °C, a perfectly normal dependence of the internal damping. $\varDelta$ on the temperature. The damping is small and almost independent of temperature, if care is taken to avoid magnetostrictive effects by placing the specimen in a magnetic field.

By heating the sample at 700 °C in an atmosphere of carefully purified hydrogen to which a small amount of carbon monoxide has been added, a small amount of carbon may be distributed homogeneously in the sample. After this treatment the sample is quenched in order to prevent the carbon from segregating in the form of a carbide. Quenching needs not be severe however to keep all of the carbon (e.g., 0.01%) in solid solution.

After the introduction of carbon the internal damping shows a pronounced maximum near room temperature. Measurements by DIJKSTRA show that the height of the maximum is directly proportional to the amount of carbon introduced. Indicating this extra damping due to carbon with the symbol $\varDelta_C$ we may say that every 0.001 percent carbon leads to an increase in $\varDelta_C$ of 0.00675, an amount, which is easily measurable.

By again heating such a sample in carefully purified hydrogen at 850 °C, the maximum can be made to disappear again. Now the first point we want to stress is the following: If the heating is continued in exactly the same atmosphere at say

[1] J. L. SNOEK, *Physica*, **6** (1939) 591.

$1000°C$, i.e., slightly above the A_3 point, a small maximum reappears.

This fact shows, that:

a. A certain amount of carbon was always present in the gas notwithstanding the high degree of purification.

b. The affinity of the γ phase to carbon is much larger than the affinity of the α phase. This is in agreement with the form of the phase diagram.

We will use these facts in a later section. We do not know where the remaining carbon came from. The fact however, that both hydrogen purified by ourselves and highly purified hydrogen from an industrial plant yielded the same result, leads us to believe that it came from certain parts of the apparatus rather than from the hydrogen itself.

On reheating below the A_3 point, the maximum again completely disappears.

We are now going to make an estimate of the maximum degree of decarburization arrived at in our experiments. Our precision allowing an effect as low as $\Delta = 0.0002$ to be detected, we must assume that by a careful treatment of high purity iron it is possible to obtain a carbon content far smaller than 0.001% in fact smaller than $0,0001\%$. This certainly is again a remarkable conclusion, a few thousandths percent being usually given as the lowest limit obtainable.

We have thought it advisable to test this result by the classical combustion method. In this laboratory an apparatus had been constructed by Dr. J. J. WENT much along the lines indicated by T. D. YENSEN [1]. Samples carefully decarburized by us were tested in it with every precaution. We need not got into details here, but only mention the general result: at first it did not seem possible to obtain results lower than $0,003\%$ By replacing the alundum crucible by a quartz vessel however, a sudden drop to $0,001\%$ was obtained. The conclusion is that the combustion test does not allow of a higher precision

[1] T. D. YENSEN, Chapter on the preparation of magnetic materials in: FR. BITTER, *Introduction to Ferromagnetism*, New York 1937.

than this and therefore measurements of the elastic after effect are the better guide at these very low concentrations.

4. *Plastic properties*. It was pointed out by E. OROWAN [1] that annealed iron when twisted around a finger does not bend into a circle, but instead of that forms a polygon. OROWAN at the time made a great point of this. From this fact as well as from some other experiments he drew the conclusion, that a pure metal may be very strong, when made entirely without flaws. It occurred to us that iron in a pure state is hard to obtain and really pure iron might not show this exceptional phenomenon. In view of the strong elastic after effect produced by small amounts of carbon and nitrogen it might even be possible that these elements had something to do with it.

Fig. 52.

Upper half: OROWAN's photograph of a twisted copper and a twisted iron wire.

Lower half: to the left a twisted wire of an iron specimen which had been carefully decarburized and denitrogenized.

To the right: the same iron after loading with about 0.003% carbon. Loading with an equal amount of nitrogen has precisely the same effect.

Experimental tests proved this conjecture to be true. In Fig. 52 OROWAN's photographs of a twisted copper and a twisted iron wire are reproduced. Below these a twisted wire of purified iron and one of iron containing 0,003% of carbon are placed. It is clear that the phenomenon is a secondary one and has something to do with the bad fit of the carbon particle in the lattice of α iron. In view of the fact that the

[1] E. OROWAN, *Proc. phys. Soc. London*, **52** (1940) 8.

phenomenon did not disappear after aging, it must be concluded that most probably some segregation had already taken place in the (air) quenched samples.

APPENDIX IV

ON THE THEORY OF THE ELASTIC AFTER-EFFECT IN IRON

by D. POLDER

This paper contains an outline of the rigorous mathematical theory [1] of the elastic after-effect in α-iron containing small amounts of carbon in solid solution; and is based on the ideas of SNOEK, given elsewhere in this book.

We use the following notation. C_x = number of x-positions occupied by C-atoms divided by the number of available x-positions, which is equal to the number of iron atoms $= N/V$ per cm³. $C_x = C_y = C_z = C_0$ in a state, in which all components of strain (e) and stress (P) are zero. $C_x - C_0 = c_x$.

In view of the cubic symmetry, the free energy is written as

$$
\begin{aligned}
F = F_0 \;+ &\tfrac{1}{2} c_{11} \left(e_{xx}{}^2 + e_{yy}{}^2 + e_{zz}{}^2\right) + c_{12} \left(e_{xx}e_{yy} + e_{yy}e_{zz} + e_{zz}e_{xx}\right) + \\
+ &\tfrac{1}{2} c_{44} \left(e_{xy}{}^2 + e_{yz}{}^2 + e_{zx}{}^2\right) + \delta \left(c_x + c_y + c_z\right)\left(e_{xx} + e_{yy} + e_{zz}\right) + \\
+ &\varepsilon \left(c_x e_{xx} + c_y e_{yy} + c_z e_{zz}\right) + \varphi \left(c_x + c_y + c_z\right)^2 + \\
+ &\tfrac{1}{2} \chi \left(c_x{}^2 + c_y{}^2 + c_z{}^2\right) - T S_m.
\end{aligned} \tag{1}
$$

The x, y and z-axes lie in the direction of the crystal axes. c_{11}, c_{12} and c_{44} are the well-known elastic constants; the terms with δ and ε account for the interaction energy between carbon and the iron crystal; the terms with φ and χ describe the mutual interaction of the carbon atoms. S_m is the entropy of mixing, which can be developed into a quadratic function of c_x, c_y and c_z if $c_0 \neq 0$.

[1] The theory is given in *Philips Res. Rep.*, **1** (1945/46) 5.

$$S_m = -\frac{Nk}{V} \sum_{i=x,y,z} C_i \ln C_i + (1 - C_i) \ln (1 - C_i) =$$

$$= -\frac{R}{2VC_0} (c_x{}^2 + c_y{}^2 + c_z{}^2), \qquad (c_x \lll 1). \tag{2}$$

From (1) we obtain:

I. The deformation of the lattice of pure α-iron $(C_0 = 0)$ due to known amounts of carbon on x, y and z-positions when all stress components are zero. F must be minimized with regard to the strain components. This applies to the tetragonal martensite, with $C_x = C_y = 0$.

We find:

$$\frac{\varepsilon}{c_{11} - c_{12}} = -\left(\frac{e_{zz} - e_{xx}}{c_z}\right)_{\text{Mart}} \tag{3}$$

II. The variations of C_x, C_y and C_z due to deformations of the crystal in which in the unstrained state $C_x = C_y = C_z = C_0 > 0$. F must be minimized with regard to c_x, c_y, and c_z, and we find

$$c_x = -\frac{\varepsilon}{3}\left(\frac{RT}{VC_0} + \chi\right)^{-1} . (2 e_{xx} - e_{yy} - e_{zz}) \tag{4}$$

III. The components of stress in terms of strain components in the case of instantaneous elasticity $(c_x = c_y = c_z = 0)$

$$\left.\begin{aligned} P_{xx} &= \frac{\partial F}{\partial e_{xx}} = c_{11}e_{xx} + c_{12}(e_{yy} + e_{zz}) \\ P_{xy} &= \frac{\partial F}{\partial e_{xy}} = c_{yy}e_{xy} \end{aligned}\right\} \tag{5}$$

IV. The components of stress in the case where the carbon atoms are free to reach the distribution corresponding to thermodynamic equilibrium (elastic after-effect included). After F is differentiated with regard to e, (4) must be substituted in the equation obtained:

$$\left.\begin{aligned} P_{xx} &= (c_{11} - za) e_{xx} + (c_{12} + a) (e_{yy} + e_{zz}) \\ P_{xy} &= c_{44}e_{xy} \end{aligned}\right\} \tag{6}$$

in which

$$a = \frac{\varepsilon^2}{3}\left(\frac{RT}{VC_0} + \chi\right)^{-1}. \tag{7}$$

We now introduce a new system of axes, ξ, η, ζ and assume that the material is in a state of simple tension, so that $F_{\zeta\zeta}$ is the only non-vanishing stress component. When α, β and γ are the cosines between ζ-axis and x, y and z-axes, we derive, following the usual procedures in the theory of elasticity, in the case of instantaneous elasticity:

$$e_{\zeta\zeta} = P_{\zeta\zeta}\left\{\frac{c_{11}+c_{12}}{(c_{11}-c_{12})(c_{11}+zc_{12})} + \right.$$
$$\left. + \left(\frac{1}{c_{44}} - \frac{2}{c_{11}-c_{12}}\right)(\alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2)\right\}. \tag{8}$$

The extension $e'_{\zeta\zeta}$, — after-effect included — is obtained if we replace in (8) c_{11} by $c_{11} - za$ and c_{12} by $c_{12} + a$.

We assume $\dfrac{a}{c_{11}-c_{12}} \ll 1$ and neglect terms with a^2. The result is

$$e'_{\zeta\zeta} - e_{\zeta\zeta} = P_{\zeta\zeta} \cdot \frac{2}{3} \cdot \left(\frac{RT}{VC_0} + \chi\right)^{-1}\left(\frac{\varepsilon}{c_{11}-c_1}\right)^2 \times$$
$$\times \left\{1 - 3\left(\alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2\right)\right\} \tag{9}$$

Now experiments show that the after-effect is directly proportional to C_0. That indicates that $\chi \ll \dfrac{RT}{VC_0}$. The final formula is found by substituting (3) into (9):

$$e'_{\zeta\zeta} - e_{\zeta\zeta} = P_{\zeta\zeta} \cdot \frac{2}{3} \cdot \frac{VC_0}{RT}\left(\frac{e_{zz}-e_{xx}}{C_z}\right)^2_{\text{Mart}}$$
$$\times \left\{1 - 3\left(\alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2\right)\right\} \tag{10}$$

Appendix V

SHAPE OF A BLOCH ZONE EXPOSED TO THE ACTION OF AN EXTERNAL FIELD H_e AND KEPT IN POSITION BY "FREEZING IN" CERTAIN SPINS.

We first treat the case where $H_e = 0$ and wish to find the way in which Θ, the angle between the spin and a certain direction along which we are to apply a magnetic field later, varies with η, the position along a line passing through the spin in a direction normal to the Bloch zone.

The calculation runs on the same lines as indicated by BECKER and DÖRING on page 191 of their book.

One easily derives for γ, the surface energy of the Bloch zone, the expression

$$\gamma = \int\limits_{-\infty}^{+\infty} \left\{ \frac{A}{4a} \cdot \left(\frac{\mathrm{d}\Theta}{\mathrm{d}\eta} \right)^2 + C \sin^2 \Theta \right\} \mathrm{d}\eta = \int\limits_{-\infty}^{+\infty} F(\Theta, \Theta') \, \mathrm{d}\eta \qquad (1)$$

where $C = \frac{3}{2} \lambda \sigma$ (λ the magnetostriction, σ the external stress) and A the exchange energy per cm³.

We require γ to be minimum and this leads to the Lagrange condition

$$\frac{\mathrm{d}}{\mathrm{d}\eta} \cdot \left(\frac{\partial F}{\partial \Theta'} \right) = \frac{\partial F}{\partial \Theta} \qquad (2)$$

Evaluating (2) and putting $\dfrac{A}{aC}$ equal to δ^2, where δ turns out to be the effective thickness of the Bloch zone, we find

$$\frac{\delta^2}{4} \cdot \frac{\mathrm{d}}{\mathrm{d}\eta} \cdot 2 \cdot \frac{\mathrm{d}\Theta}{\mathrm{d}\eta} = \frac{\mathrm{d}}{\mathrm{d}\Theta} \sin^2 \Theta \qquad (3)$$

Multiplying by $\dfrac{\mathrm{d}\Theta}{\mathrm{d}\eta}$ we find

$$\frac{\delta^2}{4} \cdot \left(\frac{\mathrm{d}\Theta}{\mathrm{d}\eta} \right)^2 = \sin^2 \Theta + C_1 \qquad (4)$$

in which C_1 may be put equal to zero. We then find the differential equation

$$\frac{\delta}{2} \cdot \frac{\mathrm{d}\Theta}{\sin \Theta} = \mathrm{d}\eta \tag{5}$$

which on integration leads to

$$\frac{\delta}{2} \ln \tan \frac{\Theta}{2} = \eta + C_2 \tag{6}$$

By choosing C_2 zero, the zero point for the ordinate

$$x = 2\frac{\eta}{\delta} \tag{7}$$

is made to fall just in the middle of the Bloch zone, i.e. in the point where Θ assumes the value $\frac{\pi}{2}$ lying midway between the extremes 0 and π.

To the right and the left of this point the curves indicating the variation of Θ with x are identical in shape (Fig. 25).

On applying an external field and keeping the boundary zone in place by an artificial means this symmetry with respect to the point where Θ equals $\frac{\pi}{2}$ is bound to disappear. Moreover we may expect $\frac{\mathrm{d}\Theta}{\mathrm{d}x}$ to assume higher values on the whole. We shall now see how the modified calculation runs. Instead of (1) we obtain

$$\gamma = \int\limits_{-\infty}^{+\infty} \left\{ \frac{\delta}{4}\left(\frac{\mathrm{d}\Theta}{\mathrm{d}\eta}\right)^2 + \sin^2 \Theta + 1 - p \cos\Theta \right\} \mathrm{d}\eta = \int\limits_{-\infty}^{+\infty} F\left(\Theta, \Theta'\right) \mathrm{d}\eta \tag{1a}$$

where

$$p = \frac{I_{\max} \cdot H_e}{C} = \frac{I_{\max} \cdot H_e}{3/2\,\lambda\,\sigma}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \tag{7}$$

H_e being the external field. This leads to

$$\frac{\delta^2}{4}\cdot\frac{\mathrm{d}}{\mathrm{d}\eta}2\frac{\mathrm{d}\Theta}{\mathrm{d}\eta}=\frac{\mathrm{d}}{\mathrm{d}\Theta}\sin^2\Theta+\frac{\mathrm{d}}{\mathrm{d}\Theta}(-p\cos\Theta) \qquad (3a)$$

instead of (3) and thus to

$$\frac{\delta^2}{4}\cdot\left(\frac{\mathrm{d}\Theta}{\mathrm{d}\eta}\right)^2=\sin^2\Theta-p\cos\Theta+C_1 \qquad (4a)$$

instead of (4). We put C_1 equal to one, because then and only then $\dfrac{\mathrm{d}\Theta}{\mathrm{d}\eta}$ becomes equal to zero, if Θ is chosen equal to zero. We find instead of (5)

$$\frac{\delta}{2}\cdot\frac{\mathrm{d}\Theta}{\sqrt{\sin^2\Theta+2p\sin^2\dfrac{\Theta}{2}}}=\mathrm{d}\eta \qquad (5a)$$

which on integration leads to

$$\frac{1}{\sqrt{1+\dfrac{p}{2}}}\cdot\ln\frac{2\tan\dfrac{\Theta}{2}}{1+\sqrt{1+\dfrac{p/2}{1+p/2}\cdot\tan^2\dfrac{\Theta}{2}}}=\frac{2\eta}{\delta}+C_2=2x+C_2 \quad (6)$$

In Fig. 25 the dotted line indicates the modified and now no longer symmetrical form of $\Theta(x)$, choosing p equal to 0.1 and $C_2=$ zero.

From the form of (5) it is immediately visible that $\dfrac{\mathrm{d}\Theta}{\mathrm{d}x}$ at the point where Θ is equal to $\dfrac{\pi}{2}$ is no longer equal to one, but that instead of that we have in first approximation

$$\frac{\mathrm{d}\Theta}{\mathrm{d}x}=\sqrt{\sin^2\Theta+2p\sin^2\frac{\Theta}{2}}=1+\frac{p}{2} \qquad (8)$$

It is of course an open question whether the shape of a Bloch zone which is exposed to the action of an external field and kept in position by artificial means has any likeness to a zone which is actually moving under the action of the field.

NOTES
added to the second edition

a *Dispersion and absorption at high frequencies*

After this book went to the press for the first time our ideas concerning the cause of what was then called the h.f. magnetic after-effect (cf. § 20) have changed considerably [1].

It has now become clear that the losses at frequencies of the order of one Mc/s are due to resonance rather than after-effect.

A spinning electron whose direction of spin does not coincide with the direction of minimum energy when left to itself performs a precessional movement round this direction.

Suppose a magnetic field H_p is the only directional force acting on the spin. The circular frequency of the precession is then given by

$$\omega_0 = |g| \cdot H_p \tag{1}$$

where
$$g = \frac{e}{mc} = 1.76 \times 10^6 \tag{2}$$

is the ratio of the magnetic moment $\dfrac{e\,h}{4\pi\,mc}$ to the mechanical moment $\frac{1}{2} \cdot \dfrac{h}{2\pi}$.

For a sphere which is magnetized to saturation by a sufficiently strong field H_p, equation (1) is wholly correct. For an ellipsoid modifications have to be introduced due to the circumstance that the demagnetizing factor N and accordingly the total internal magnetic energy is now a function of the direction of magnetization.

Equation (1) is found to change into the self-evident form:

$$\omega_0 = |g| \left[\Big\{ H_p + (N_x - N_z) M \Big\} \Big\{ H_p + (N_y - N_z) M \Big\} \right]^{\frac{1}{2}} \quad (3)$$

In this equation N_z is the demagnetizing factor along the main axis of the ellipsoid coinciding with the direction of H_p. N_x and N_y are the demagnetizing factors for the two other main axes and M the saturation magnetization.

Calculations show that a weak magnetic field of frequency $\omega \sim \omega_0$ when applied in a direction at right angles to H_p tends to excite this precessional movement to an amount depending of course on $\omega - \omega_0$ and further on the internal damping. Neglecting the influence of the latter it is found that the component of the magnetization in the direction of the applied field in the neighbourhood of ω_0 is increased with respect to the static value in the ratio $x(\omega)$, which is given by the equation

$$x(\omega) = \frac{1}{1 - \left(\dfrac{\omega}{\omega_0}\right)^2} \quad (4)$$

Large positive and large negative values may thus be expected for values of ω just below and just above ω_0. For $\omega \gg \omega_0$ the magnetization decreases proportional to ω^{-2}. The essence of these facts has already been verified on thin sheets of ferro-magnetic metals [2]. It remains to be explained what all this has to do with magnetic losses observed in samples of ferrite in the absence of any polarizing field.

The answer is that in such samples the anisotropy field takes over the role of the polarizing field, in providing the required directional force [3].

For a specimen having uniaxial symmetry and being magnetized at right angles to the direction of minimum energy one easily derives

$$\omega_0 = |g| \frac{M}{\chi_0} \quad (5)$$

where χ_0 is the observed static value of the susceptibility.

Equation (5) suffers only minor changes when adapted for use with polycrystalline aggregates having a cubic structure

such as have the ferrites studied by us. One may expect that

always $\omega_{obs} < \omega_0$ (6)

and this is actually found in experiment.

The reciprocal relation between ω_0 and X_0 as given by (5) is highly satisfactory because it is what general experience seems to indicate.

It remains for the future to work out the details of the facts connected with the change of the permeability with frequency as observed in the ferrites.

b *Neel's criticism of the Becker-Kersten theory*

L. NEEL [4] has drawn the attention to the fact that BECKER as well as KERSTEN leave completely out of account the internal energy created inside a ferromagnetic sample, if the condition that the normal component of the magnetization shall not be changed on passing through a BLOCH boundary zone is violated.

In general we must expect that every unmagnetic or weakly magnetic inclusion, the size of which passes a certain critical value gives rise to new domains in the immediate neighbourhood of this inclusion.

KERSTEN's model is also too simple in that the distribution of the inclusions is assumed to be strictly periodical.

The new formulae derived by NEEL are very complicated and at this moment preclude a satisfactory discussion.

It is highly satisfactory, however, that the additional WEISS domains expected to occur near an unmagnetic inclusion have been since observed in the Laboratory of the Bell Telephone Company by means of the magnetic colloid method [5].

Eindhoven, July 20th 1948

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Birth: 1904
              Utrecht, Netherlands
Death: Dec. 3, 1950
              Shaker Heights
              Cuyahoga County
              Ohio, USA

Taken from: Kokomo Tribune
              December 4, 1950
              Front page (top centre)

NOTED DUTCH METAL EXPERT CRASH VICTIM
Dr. Jacob Snoek Killed at Elkhart in Auto Accident
(By The Associated Press)

A well-known Dutch expert on metals was one of the 12 persons killed in Indiana's weekend traffic accidents.

Dr. Jacob L. Snoek, 46, of Shaker Heights, O., died in Elkhart General hospital last evening two hours after his car hit an icy spot on U.S. 6 about 2½ miles west of Nappanee. Dr. Snoek and John McGrath, 23, of Cleveland, both employees of Horizons, Inc., were on their way from Cleveland to the Horizons research plant in Valparaiso. McGrath was not injured seriously and may be dismissed from the hospital today. The top of the car was sheared off by a steel railroad rail which was used as a fencepost. Dr. Snoek's body was taken to Melbourn and Sons funeral home in Cleveland. Burial will be in Lakeview Cemetery. He was born in Utrecht, Holland.

In U.S. Since April

Dr. Snoek came to this country last April to become head physicist for Horizons, which does research work in metallurgy, physics, ceramics and chemistry. He studied at the University of Utrecht in Europe and had written many scientific articles on solid state physics and ferromagnetism. He is survived by a widow and a son.

Burial:
Lake View Cemetery
Cleveland
Cuyahoga County
Ohio, USA
Plot: Section 53   Lot 5-22